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(54) POSITIVE PHOTOSENSITIVE COMPOSITION

(57)Abstract:

PURPOSE: To provide a positive photosensitive composition which realizes reduced wear of the film at the time of performing the development and has high sensitivity and high resolving power and also gives good profiles.

CONSTITUTION: The positive photosensitive composition contains (a) a resin that is insoluble in water but soluble in alkali aqueous solutions, (b) a compound that generates acid by irradiating it with actinic or radioactive rays and (c) a low molecular weight, acid-decomposable, dissolution-inhibitory compound which has a ≤3000 molecular weight and contains acid-decomposable groups, and the solubility of which in the alkali developer is increased by the action of acid. The compound (c) features in that it is at least one compound selected from among (i) compounds that contains at least two per molecule acid- decomposable groups, each of adjacent two of which has at least ten bonding atoms other than the acid-decomposable groups between them when the distance between the adjacent two acid-decomposable groups is the longest, and (ii) compounds that contains at least three per molecule acid-decomposable groups, each of adjacent two of which has at least nine bonding atoms other than acid-decomposable groups between them when the distance between the adjacent two acid-decomposable groups is the longest.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1](a) A compound which is insoluble in water and generates acid by the exposure of meltable resin, (b) active light, or radiation in an alkaline aqueous solution, . And have a basis which may be decomposed with (c) acid and solubility in inside of an alkali developing solution increases by operation of acid. In a with a molecular weight of 3,000 or less low molecule acidolysis nature lysis inhibition compound and a positive type photosensitive composition containing a solvent which can dissolve (d) and (a) – (c), In a position which has at least two bases which this compound (c) may decompose from (i) acid, and distance between these acidolysis nature groups left most, In a position which has a compound which goes via ten or more joint atoms except an acidolysis nature group, and at least three bases which may be decomposed from (ii) acid, and distance between these acidolysis nature groups left most, a compound which goes via nine or more joint atoms except an acidolysis nature group, and ********** -- a positive type photosensitive composition having a solvent whose (d) it is one sort even if small, and is 130–155 ** of boiling points at least 30% of the weight among all the solvents.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application]This invention relates to the positive type photosensitive composition used for manufacture of the circuit boards, such as semiconductor manufacturing processes, such as a lithography board and IC, a liquid crystal, and a thermal head, and also other photofabrication processes.

[0002]

[Description of the Prior Art]As a positive type photoresist composition, the constituent which generally contains alkalis soluble resin and the naphthoquinonediazide compound as a sensitization thing is used. As "novolac type phenol resin / a naphthoquinonediazide substituted compound", for example, U.S. Pat. No. 3,666,473, To U.S. Pat. No. 4,115,128, U.S. Pat. No. 4,173,470, etc. As most typical constituent. The example of "the novolak resin / trihydroxy benzophenone 1,2–naphthoquinonediazide sulfonic ester" which comprises cresol formaldehyde Thompson "introduction two micro lithography." (L. F.Thompson "Introduction toMicrolithography") It is indicated (ACS publication, No.2 19 No., p112–121). As for such positive type photoresist that comprises novolak resin and a quinone diazide compound fundamentally, novolak resin gives high tolerance to plasma etching, and a naphthoquinonediazide compound acts as a lysis inhibition agent. And when an optical exposure is received, by producing carboxylic acid, naphthoquinonediazide loses lysis inhibition ability and has the characteristic of raising the alkali solubility of

novolak resin.

[0003]From this viewpoint, much positive type photoresist containing novolak resin and a naphthoquinonediazide system sensitization thing was developed and put in practical use, and has so far stored sufficient result in line width processing up to 0.8 micrometer - about 2 micrometers. However, the integrated circuit is raising the degree of location increasingly, and processing of a super-minute pattern which comprises the line width below a half micron in manufacture of semiconductor substrates, such as very large scale integration, has come to be needed. In order to attain this required resolution, the using wavelength of the exposure device used for photo lithography is short-wave-ized increasingly, and by the time far ultraviolet light and excimer laser beams (XeCl, KrF, ArF, etc.) are examined, now, it will become. If the resist which comprises conventional novolac and naphthoquinonediazide compound is used for the pattern formation of the lithography using far ultraviolet light or an excimer laser beam, Since the absorption in the far ultraviolet region of novolac and naphthoquinonediazide is strong, light becomes difficult to reach to a resist pars basilaris ossis occipitalis, and only the pattern which attached the taper with low sensitivity is obtained.

[0004]One of the means to solve such a problem is the chemical amplification system resist composition indicated to U.S. Pat. No. 4,491,628, European patent No. 249,139, etc. A chemical amplification system positive resist composition is a pattern formation material which makes an exposure part generate acid by the exposure of radiation, such as far ultraviolet light, changes the solubility over the developing solution of the irradiation part of active radiation, and a non-irradiation part, and makes a pattern form on a substrate by the reaction which makes this acid a catalyst.

[0005]The combination of the compound which generates acid by a photolysis as such an example, and acetal or O, and N-acetal compound (JP,48-89003,A), Ortho ester or combination with an amide acetal compound (JP,51-120714,A), Combination with the polymer which has an acetal or a ketal group in a main chain (JP,53-133429,A), Combination with an enal ether compound (JP,55-12995,A), Combination with N-acyl imino carbonate compound compound (JP,55-126236,A), Combination with the polymer which has an ortho ester group in a main chain (JP,56-17345,A), Combination (JP,60-3625,A) with the 3rd class alkyl ester compound, combination (JP,60-10247,A) with a silyl ester compound, combination (JP,60-37549,A, JP,60-121446,A) with a silyl ether compound, etc. can be mentioned. These show high photosensitivity, in order that a quantum yield may exceed 1 theoretically.

[0006]Similarly, although it is stable under room temperature temporality, By heating under acid existence, decompose and as a system which carries out alkali solubilization, For example, JP,59-45439,A, JP,60-3625,A, JP,62-229242,A, JP,63-27829,A, JP,63-36240,A, JP,63-250642,A, Polym.Eng.Sce., 23 volumes, 1012 page (1983);ACS.Sym.242 volume, 11 pages (1984); Semiconductor World 1987, The November item, 91 page;Macromolecules, 21 volumes, 1475 pages (1988); The compound which generates acid by exposure indicated to SPIE, 920 volumes, 42 pages (1988), etc., Ester of the 3rd class or the 2nd class carbon (for example, t-butyl, 2-cyclohexenyl) or a combination system with a carbonic ester compound is mentioned. These systems also have high sensitivity and absorption in a Deep-UV range can serve as a system effective in the aforementioned light source short wavelength formation from a small thing compared with naphthoquinonediazide / novolak resin system.

[0007]Three component systems to which the above-mentioned positive type chemical amplification resist

changes from alkalis soluble resin, the compound (photo-oxide generating agent) which generates acid by radiation exposure, and the lysis inhibition compound to the alkalis soluble resin in which it has an acidolysis nature group, It can divide roughly into the two-component system which consists of resin which has a basis which decomposes by a reaction with acid and serves as alkali soluble, and a photo-oxide generating agent. The problem that a resist film contracts by the bake after exposure since the content of the acidolysis group in resin increases in the case of the two-component system is ******. The problem that the film decrease at the time of development is large, and degrades a resist profile remarkably on the other hand since three component systems of the lysis inhibition nature to alkalis soluble resin are insufficient is ******. However, three component systems are promising systems from the width of raw material selection being large.

Development of the acidolysis nature compound which is used for this system and which was excellent in lysis inhibition nature was desired.

[0008]

[Problem(s) to be Solved by the Invention]Therefore, the purpose of this invention improves the above-mentioned problem, and there is little film decrease at the time of development, and it is providing the positive type photosensitive composition which has high sensitivity, high resolving power, and a good profile.

[0009]

[Means for Solving the Problem]In a positive type chemical amplification system which comprises a lysis inhibition compound and a solvent in which the purpose of this invention has alkalis soluble resin, a photo-oxide generating agent, and an acidolysis nature group as a result of this invention persons' inquiring wholeheartedly with careful attention to the above-mentioned various characteristics, It found out being attained by using a solvent of the following requirements as a solvent using a low molecule acidolysis nature lysis inhibition compound which satisfies requirements shown below as a lysis inhibition compound, and this invention was reached. namely, this invention -- (a) -- a compound which is insoluble in water and generates acid by the exposure of meltable resin, (b) active light, or radiation in an alkaline aqueous solution. . And have a basis which may be decomposed with (c) acid and solubility in inside of an alkali developing solution increases by operation of acid. In a with a molecular weight of 3,000 or less low molecule acidolysis nature lysis inhibition compound and a positive type photosensitive composition containing a solvent which can dissolve (d) and (a) - (c), In a position which has at least two bases which this compound (c) may decompose from (i) acid, and distance between these acidolysis nature groups left most, In a position which has a compound which goes via ten or more joint atoms except an acidolysis nature group, and at least three bases which may be decomposed from (ii) acid, and distance between these acidolysis nature groups left most, a compound which goes via nine or more joint atoms except an acidolysis nature group, and ********** -- even if small, it is one sort, and a positive type photosensitive composition having a solvent whose (d) is 130-155 ** of boiling points at least 30% of the weight among all the solvents is provided.

[0010]Fundamentally, 3 component-system positive type photosensitive composition of this invention comprises an acidolysis nature dissolution inhibitor, alkalis soluble resin, and a photo-oxide generating agent.

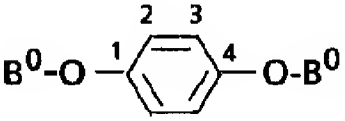
Deprotection of the acidolysis nature group is carried out with acid by which it will be generated if an acidolysis nature dissolution inhibitor controls solubility to alkali of alkalis soluble resin and receives exposure, and it has the operation which promotes solubility to alkali of resin conversely. Although a dissolution control compound which uses naphthalene, biphenyl, and diphenyl cycloalkane as a skeleton compound at JP,63-27829,A and JP,3-198059,A is indicated, lysis inhibition nature to alkalis soluble resin is small, and insufficient in respect of a profile and resolution. Hereafter, a compound used for this invention is explained in detail.

[0011](A) Acidolysis nature lysis inhibition compound (compound of this invention (c))

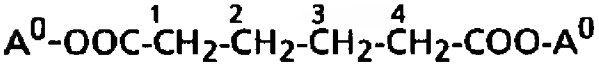
An acidolysis nature lysis inhibition compound used for this invention (c), In a position which has at least two bases which may be decomposed from acid into the structure, and distance between these acidolysis nature groups left most, In a position which has at least ten pieces, a compound via which it goes at least 12 pieces still more preferably at least 11 pieces preferably, or at least three acidolysis nature groups for a joint atom except an acidolysis nature group, and distance between these acidolysis nature groups left most, They are at least nine pieces and a compound via which it goes at least 11 pieces still more preferably at least ten pieces preferably about a joint atom except an acidolysis nature group. The number of 50 desirable maximums of the above-mentioned joint atom is 30 still more preferably. In this invention, when an acidolysis nature lysis inhibition compound has preferably three or more acidolysis nature groups [four or more], and when separated [beyond fixed distance that has this acidolysis nature group mutually] also in what has two acidolysis nature groups, lysis inhibition nature to alkalis soluble resin improves remarkably. Distance between acidolysis nature groups in this invention is shown by course joint atomic number excluding an acidolysis nature group. For example, in the case of the following compounds (1) and (2), distance between acidolysis nature groups is four joint atoms respectively, and is 12 joint atoms with a compound (3).

[0012]

[Formula 1]



(1)



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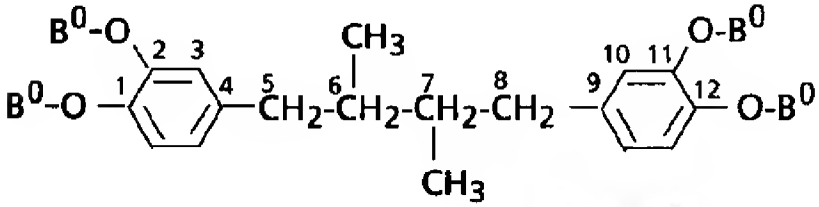


(3)

酸分解性基：-COO-A^0, -O-B^0

[0013]As for this invention, it is preferably preferred [50 mol %] 30-mol% among all the content of the compound of this invention (c) that it is the compound which made the alkali solubility group remain

intentionally still more preferably at least 10-mol%. the content of an alkali solubility group -- several N_S of the alkali solubility group of the average in the 3rd class alkyl ester group content dissolution inhibitor, and several N_B of the average 3rd class alkyl ester group -- a table -- the bottom can express with $N_S/(N_B+N_S)$. As a quantity of an alkali solubility group, $0.01 <= N_S/(N_B+N_S) <= 0.75$ is preferred. It is $0.1<=N_S/(N_B+N_S) <=0.5$ preferably. Preferably especially the ratio of the number of the alkali solubility groups in one molecule of dissolution inhibitors (N_{1S}) to the 3rd class alkyl ester group (N_{1B}), It is a case where dissolution inhibitor full weight contains the constituent which is $0.1<=N_{1S}/(N_{1B}+N_{1S}) <=0.5$ 50% of the weight or more.

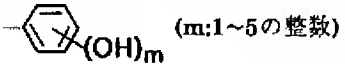
[0014]As for an alkali solubility group and an alkali solubility group made to remain which are protected by acidolysis nature combination, in order that an alkali solubility group may function with a developing solution mentioned later, it is preferred that pK_a is ten or less basis. As a desirable alkali solubility group, a phenolic hydroxyl group, a carboxylic acid group, A basis which has an imido group, an N-hydroxy imido group, N-sulfonyl amide group, a sulfonamide group, N-sulfonyl urethane group, N-sulfonyl ureido group, or an active methylene group can be mentioned, and, more specifically, the following examples can be given.

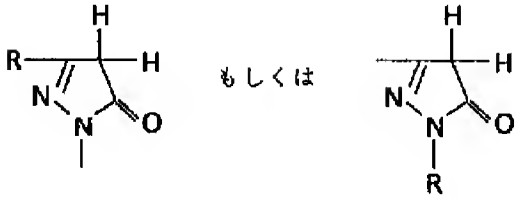
[0015]

[Formula 2]

-COOH、-SO_3H、-SO_2H、-$COCH_2COR$、-$CONHSO_2R$、

-SO_2NHR、-$SO_2NHCONHR$、-$SO_3NHCOOR$、

-$NHSO_2NHCOR$、  (m:1～5の整数)



(R:アルキル基もしくはアリール基)

[0016]These bases may be mixed and introduced into one molecule. However, a desirable alkali solubility group is not limited to these examples.

[0017]Although the acidolysis nature lysis inhibition compound of this invention may have two or more acidolysis nature groups on the one benzene ring, it is a compound which comprises preferably a skeleton which has one acidolysis nature group on the one benzene ring. furthermore -- the molecular weight of the acidolysis nature lysis inhibition compound of this invention is 3,000 or less -- desirable -- 500-3,000 -- it is 1,000-2,500 still more preferably.

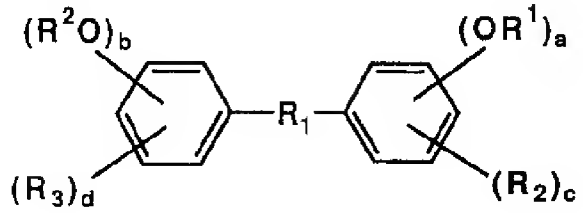
[0018]In a desirable embodiment of this invention, a basis shown by $-R^0-COO-A^0$ or $-Ar-O-B^0$ is mentioned as a basis containing basis-$COO-A^0$ and a $-O-B^0$ group which may be disassembled with acid. A^0 shows $-C(R^{01})(R^{02})(R^{03})$, $-Si(R^{01})(R^{02})(R^{03})$, or a $-C(R^{04})(R^{05})-O-R^{06}$ group here. B^0 shows A^0 or a $-CO-O-A^0$ group. R^{01}, R^{02}, R^{03}, R^{04}, and R^{05}, It may be the same respectively, or difference may be carried out, a hydrogen atom, an alkyl group, a cycloalkyl group, an alkenyl group, or an aryl group is shown, and R^{06} shows an alkyl group or an aryl group. However, at least two of R^{01} - R^{03} are bases other than a hydrogen atom, and two bases in R^{01} - R^{03} and R^{04} - R^{06} may join together, and they may form a ring. R^0 shows aliphatic series or an aromatic

hydrocarbon group more than divalent [which may have a substituent], and -Ar- shows an aromatic group more than divalent [which may have a substituent of a monocycle or many rings].
[0019]As an alkyl group here A methyl group, an ethyl group, a propyl group, n-butyl group, A thing of 1-4 carbon numbers like a sec-butyl group and t-butyl group is preferred, As a cycloalkyl group, a cyclopropyl group, a cyclobutyl group, a cyclohexyl group, A thing of 3-10 carbon numbers like an adamanthyl group is preferred, and as an alkenyl group A vinyl group, A thing of 2-4 carbon numbers like a propenyl group, an allyl group, and a butenyl group is preferred, and a thing of 6-14 carbon numbers like a phenyl group, a xylyl group, a toluyl group, a KUMENIRU group, a naphthyl group, and an anthracenyl group as an aryl group is preferred. moreover -- as a substituent -- a hydroxyl group and a halogen atom (fluoride, chlorine, and bromine.) Iodine, a nitro group, a cyano group, the above-mentioned alkyl group, a methoxy group, an ethoxy basis, a hydroxyethoxy basis, a propoxy group, a hydroxy propoxy group andn - Alkoxy groups, such as a butoxy group, an isobutoxy group, a sec-butoxy group, and t-butoxy group, Alkoxycarbonyl groups, such as a methoxycarbonyl group and an ethoxycarbonyl group, Aralkyl groups, such as benzyl, a phenethyl group, and a cumyl group, an aralkyloxy group, Acyl groups, such as a formyl group, an acetyl group, a butyryl group, benzoyl, a SHIANAMIRU group, and a valeryl group, Alkenyloxy groups, such as acyloxy groups, such as a butyryloxy group, the above-mentioned alkenyl group, a vinyloxy group, a propenyloxy group, an allyloxy group, a butenyloxy group, Aryloxy carbonyl groups, such as aryloxy groups, such as the above-mentioned aryl group and a phenoxy group, and a benzoyloxy group, can be mentioned.
[0020]Preferably, they are a silyl ether group, a cumyl ester group, an acetal group, a tetrahydropyranyl ether group, an enal ether group, an enal ester group, an alkyl ether group of the 3rd class, an alkyl ester group of the 3rd class, an alkyl carbonate group of the 3rd class, etc. They are the 3rd class alkyl ester group, the 3rd class alkyl carbonate group, a cumyl ester group, and a tetrahydropyranyl ether group preferably.
[0021]Preferably JP,1-289946,A, JP,1-289947,A, JP,2-2560,A, JP,3-128959,A, JP,3-158855,A, JP,3-179353,A, JP,3-191351,A, JP,3-200251,A, JP,3-200252,A, JP,3-200253,A, JP,3-200254,A, JP,3-200255,A, JP,3-259149,A, JP,3-279958,A, JP,3-279959,A, JP,4-1650,A, JP,4-1651,A, JP,4-11260,A, JP,4-12356,A, JP,4-12357,A, Japanese Patent Application No. No. 33229 [three to], Japanese Patent Application No. No. 230790 [three to], Japanese Patent Application No. No. 320438 [three to], Japanese Patent Application No. No. 25157 [four to], Japanese Patent Application No. No. 52732 [four to], Japanese Patent Application No. No. 103215 [four to], Japanese Patent Application No. No. 104542 [four to], Japanese Patent Application No. No. 107885 [four to], Japanese Patent Application No. No. 107889 [four to], A compound which combined a part or all of a phenolic OH radical of a polyhydroxy compound that was written in specifications, such as 4-152195, with a basis shown above, $-R^0-COO-A^0$, or B^0 group, and was protected is contained.
[0022]Preferably JP,1-289946,A, JP,3-128959,A, JP,3-158855,A, JP,3-179353,A, JP,3-200251,A, JP,3-200252,A, JP,3-200255,A, JP,3-259149,A, JP,3-279958,A, JP,4-1650,A, JP,4-11260,A, JP,4-12356,A, JP,4-12357,A, Japanese Patent Application No. No. 25157 [four to], A thing using Japanese Patent Application No. No. 103215 [four to], Japanese Patent Application No. No. 104542 [four to], Japanese Patent Application No. No. 107885 [four to], Japanese Patent Application No. No. 107889 [four to], and a polyhydroxy compound written in a specification of 4-152195 is mentioned.

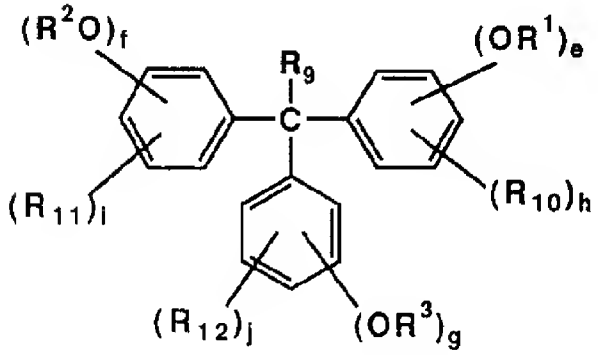
[0023]More specifically, a compound expressed with general formula [I] – [XVI] is mentioned.

[0024]

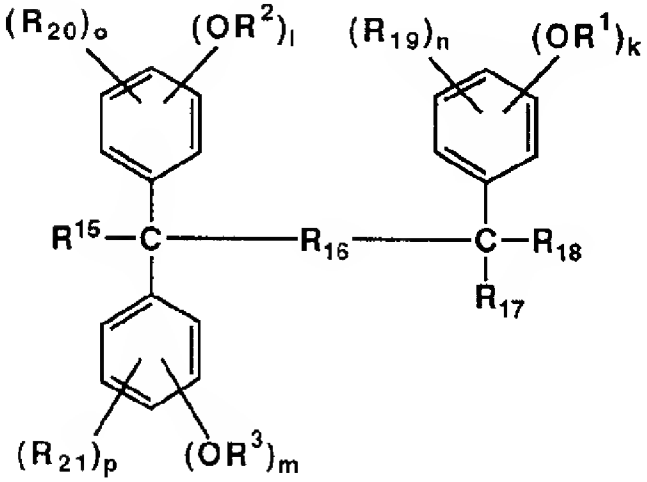
[Formula 3]



[I]



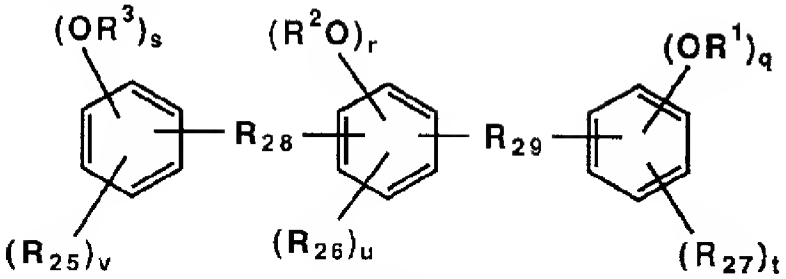
[II]



[III]

[0025]

[Formula 4]



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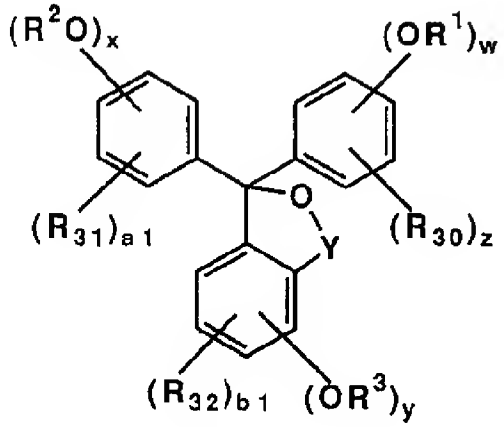
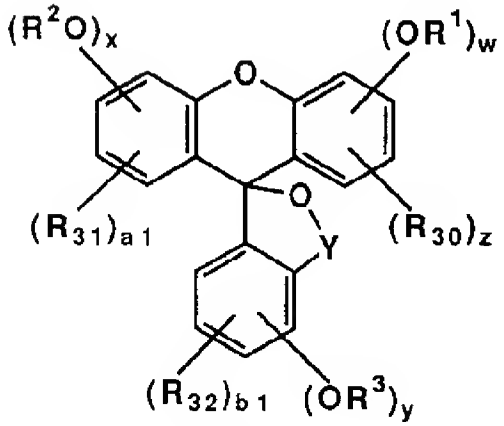


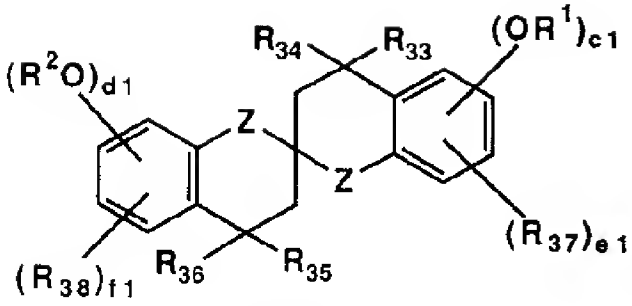
[V]



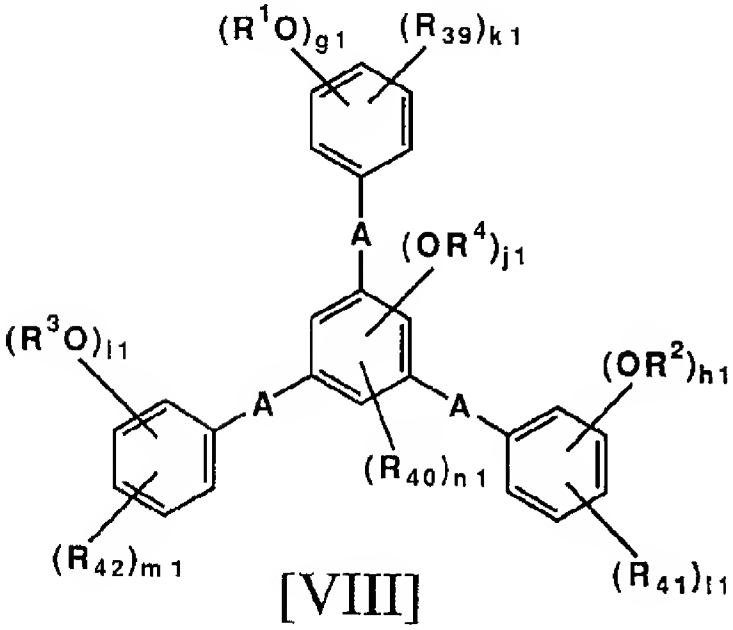
[VI]

[0026]

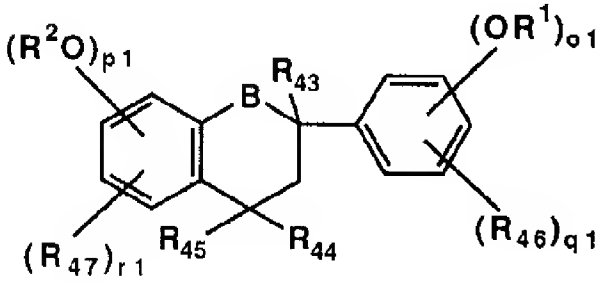
[Formula 5]



[VII]



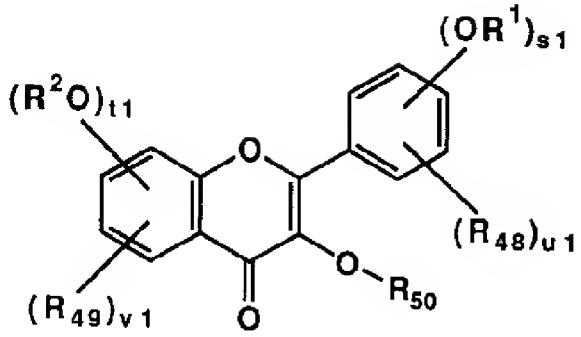
[VIII]



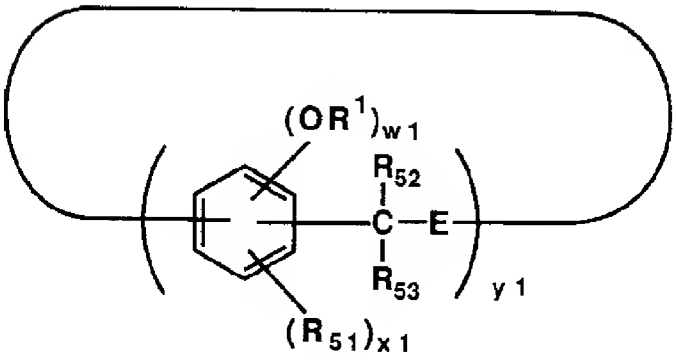
[IX]

[0027]

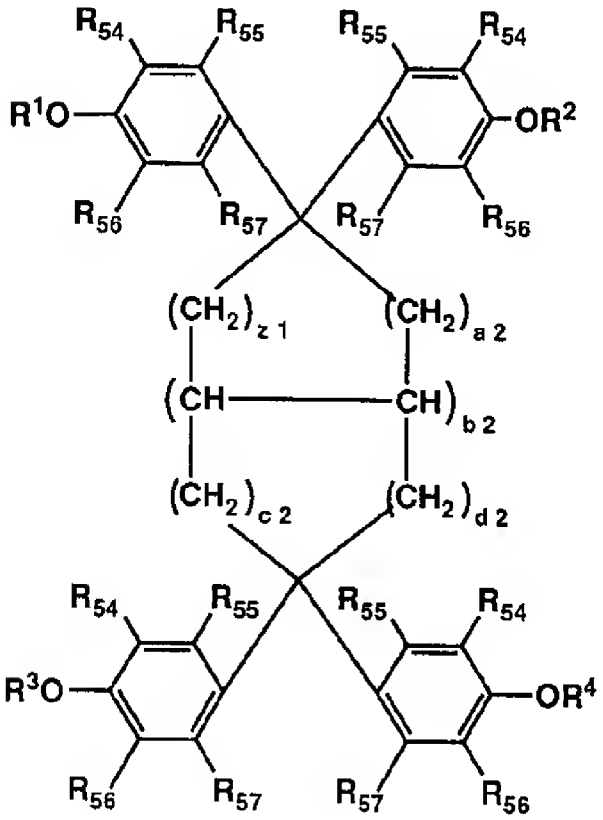
[Formula 6]



[X]



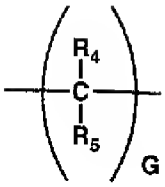
[XI]



[XII]

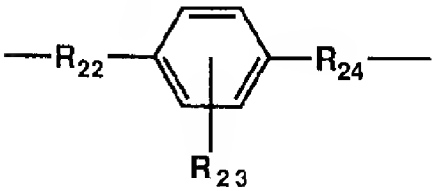
[0028]here -- R^1-R^6: -- it being the same, or differing and, a hydrogen atom, $-R^0-COO-A^0$ or B^0 group, R_1:-CO-, -COO-, -NHCONH-, -NHCOO-, and - O-, -S-, -SO-, -SO2-, and -SO3- or [0029]

[Formula 7]



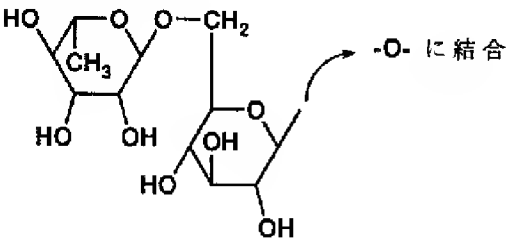
[0030]At least one side among R_4 and R_5 here at the time of G= 2-6, however G= 2 An alkyl group, R_4, R_5 : It may be the same, or may differ and A hydrogen atom, an alkyl group, an alkoxy group, -OH, -COOH, -CN, a halogen atom, $-R_6-COOR_7$, or $-R_8-OH$, R_6, an R_8:alkylene group, R_7 : A hydrogen atom, an alkyl group, an aryl group, or an aralkyl group, R_2, R_3, R_9 - R_{12}, R_{15}, R_{17} - R_{21}, R_{25} - R_{27}, R_{30} - R_{32}, R_{37} - R_{42}, R_{46} - R_{49}. And R_{51} : It may be the same or may differ, A hydrogen atom, a hydroxyl group, an alkyl group, an alkoxy group, an acyl group, an acyloxy group, an aryl group, an aryloxy group, an aralkyl group, an aralkyloxy group, a halogen atom, a nitro group, a carboxyl group, a cyano group, or -N (R_{13}). (R_{14}) (R_{13}, R_{14}:H, an alkyl group, or an aryl group). R_{16}: -- a single bond and an alkylene group -- or [0031]

[Formula 8]



[0032]R_{22}, R_{24} : It may be the same, or may differ and A single bond, an alkylene group, -O-, -S-, -CO-, or a carboxyl group, R_{23} : A hydrogen atom, an alkyl group, an alkoxy group, an acyl group, an acyloxy group, an aryl group, a nitro group, a hydroxyl group, a cyano group, or a carboxyl group, . However, hydrogen of the hydroxyl group may be replaced by $-R^0-COO-A^0$ or B^0 group. R_{28}, R_{29} : It may be the same, or may differ and A methylene group, a low-grade alkylation methylene group, a halo methylene group, or a halo alkyl group, . However, in this application, a low-grade alkyl group refers to the alkyl group of the carbon numbers 1-4. R_{33} - R_{36} : It may be the same, or may differ and A hydrogen atom or an alkyl group, R_{43}-R_{45}: -- it may be the same or may differ -- a hydrogen atom, an alkyl group, an alkoxy group, an acyl group or an acyloxy group, an R_{50}:hydrogen atom, and a t-butoxycarbonyl group -- or[0033]

[Formula 9]

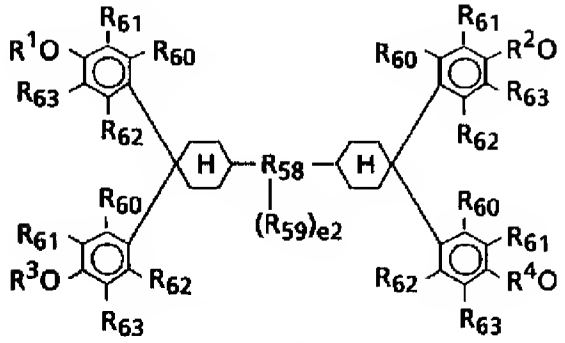


[0034]R_{52}, R_{53} : It may be the same, or may differ and A hydrogen atom, low-grade alkyl group, and low-grade halo alkyl group or an aryl group, R_{54} - R_{57} : It may be the same or may differ, A hydrogen atom, a hydroxyl group, a halogen atom, a nitro group, a cyano group, a carbonyl group, an alkyl group, an alkoxy group, an alkoxycarbonyl group, an aralkyl group, an aralkyloxy group, an acyl group, an acyloxy group, an alkenyl group, an alkenyloxy group, an aryl group, an aryloxy group, . Or an aryloxy carbonyl group, however the substituent

of the four same signs each may not be the same bases. −CO− or $-SO_2-$, Z, B : Y: A single bond or −O−, A: A methylene group, a low−grade alkylation methylene group, a halo methylene group, or a halo alkyl group, A single bond or a oxymethylene group, a−z, a1−y1 : E: At the time of plurality. () The integer of a−q and s from which the inner basis may be the same as or different, t, v, g1−i1, k1−m1, o1, q1, s1, u1:0, or 1−5, r, u, w, x, y, z, a1−f1, p1, r1, t1, v1−x1:0, or the integer of 1−4, j1, n1, z1, a2, b2, c2, d2:0, or the integer of 1−3, At least one of z1, a2, c2, and d2 1 or more, the integer of y1:3 − 8, (a+b), (e+f+g), (k+l+m), (q+r+s), (w+x+y), (c1+d1), (g1+h1+i1+j1), (o1+p1), >=(s1+t1) 2, <=(j1+n1) 3, (r+u), (w+z), (x+a1), (y+b1), (c1+e1), (d1+f1), In (p1+r1), (t1+v1), <=(x1+w1) 4, however general formula [V], (w+z), (x+a1) <=5, (a+c), (b+d), (e+h), (f+i), (g+j), (k+n), (l+o), (m+p), (q+t), (second+v), (g1+k1), (h1+l1), (i1+m1), (o1+q1), and <=(s1+u1) 5 are expressed.

[0035]

[Formula 10]

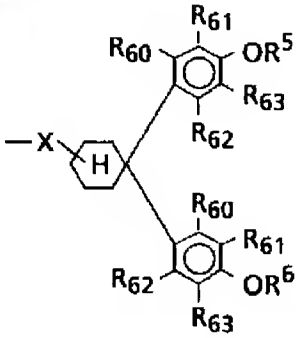


(XIII)

ここで、

R_{58} ：有機基、単結合、-S-、-SO-もしくは 

R_{59} ：水素原子、一価の有機基もしくは



R_{60}〜R_{63}：同一でも異なっていても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、アルケニル基、但し、少なくとも2つは $-O-R^0-COO-A^0$基もしくは $-O-B^0$基である、又、各4もしくは6個の同一記号の置換基は同一の基でなくても良い、

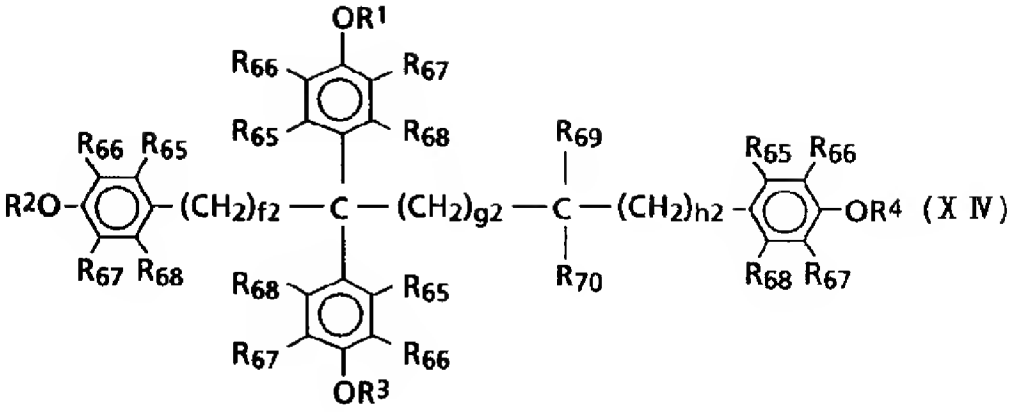
X ：2価の有機基、

e2 ：0もしくは1、

を表す。

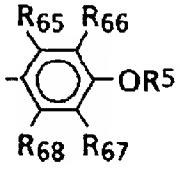
[0036]

[Formula 11]



ここで、

R_{65}~R_{68}：同一でも異なっても良く水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基もしくはアルケニル基、但し、各4~6個の同一記号の置換基は同一の基でなくても良い、

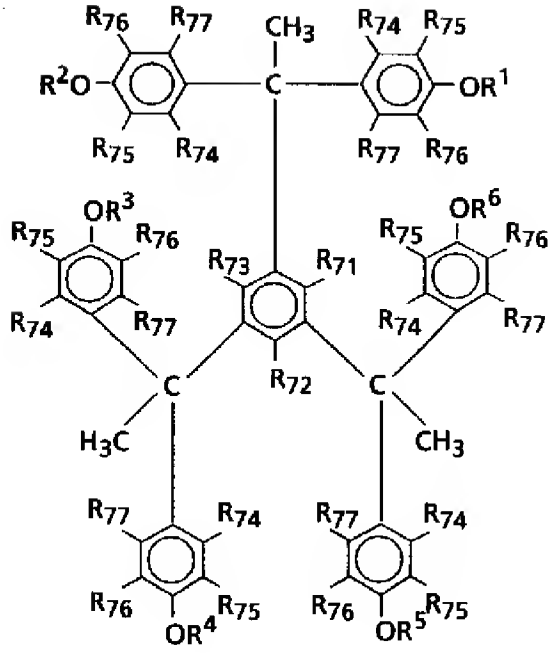
R_{69}, R_{70} ：水素原子、アルキル基もしくは 

f2, g2, h2：0もしくは1~5の整数、

を表す。

[0037]

[Formula 12]



(XV)

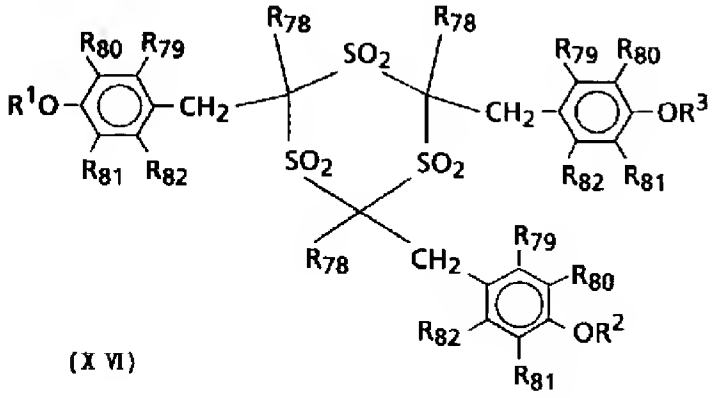
ここで、

R_{71}~R_{77}:同一でも異なっても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、ニトロ基、アルケニル基、アリール基、アラルキル基、アルコキシカルボニル基、アリールカルボニル基、アシロキシ基、アシル基、アラルキルオキシ基もしくはアリールオキシ基、但し、各6個の同一記号の置換基は同一の基でなくても良い、

を表す。

[0038]

[Formula 13]



(XVI)

ここで、

R_{78} :水素原子もしくはアルキル基、但し、全部同一でなくても良い、

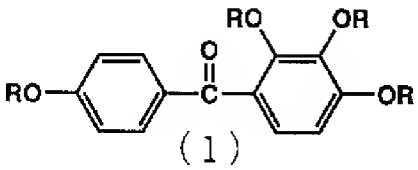
R_{79}~R_{82}:水酸基、水素原子、ハロゲン原子、アルキル基もしくはアルコキシ基、但し、各3個の同一記号の置換基は同一の基でなくても良い、

を表す。

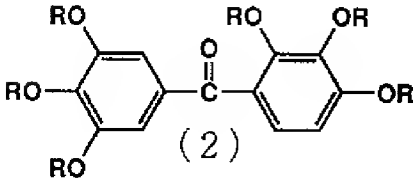
[0039]An example of a desirable compound skeleton is shown below.

[0040]

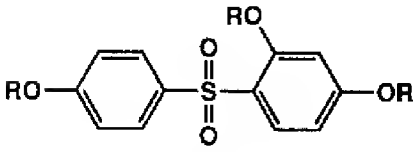
[Formula 14]



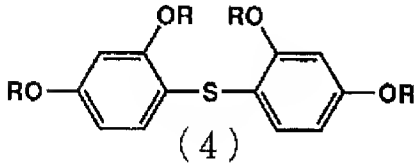
(1)



(2)



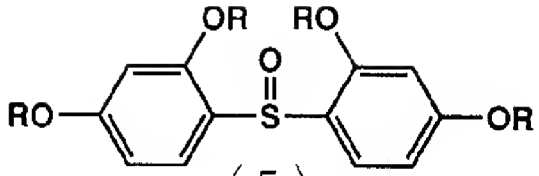
(3)



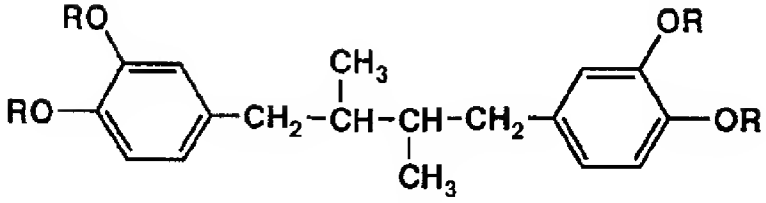
(4)

[0041]

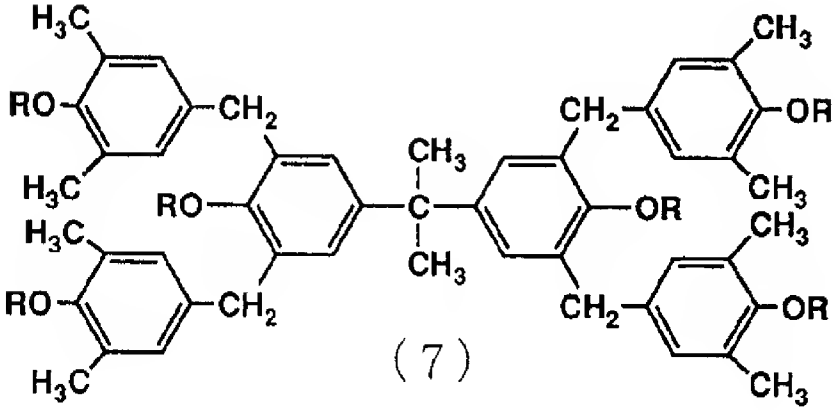
[Formula 15]



(5)



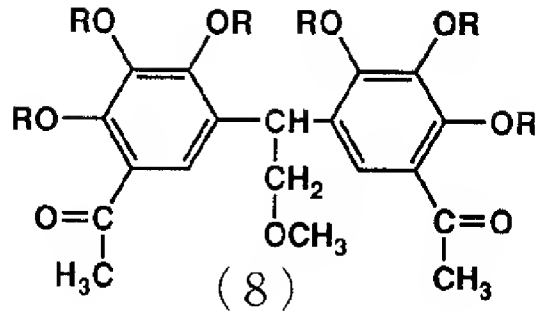
(6)



(7)

[0042]

[Formula 16]



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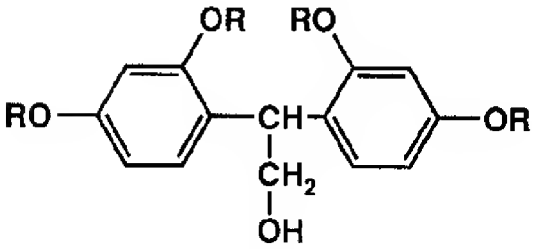
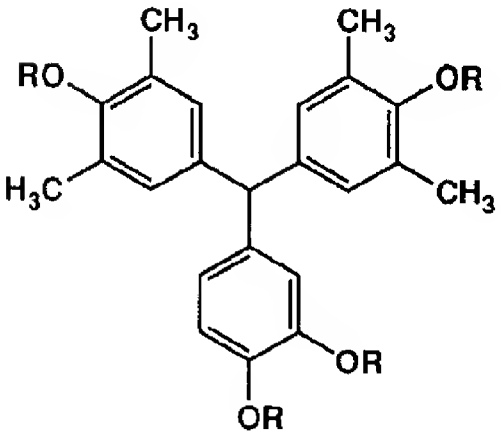


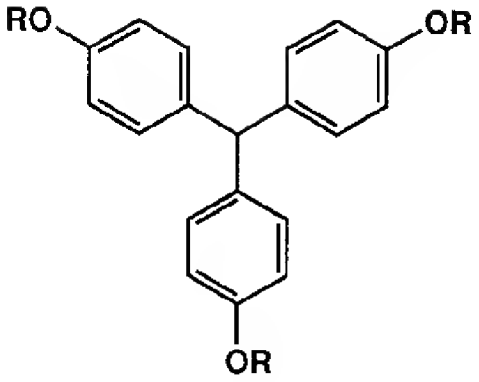
(9)



(10)

[0043]

[Formula 17]



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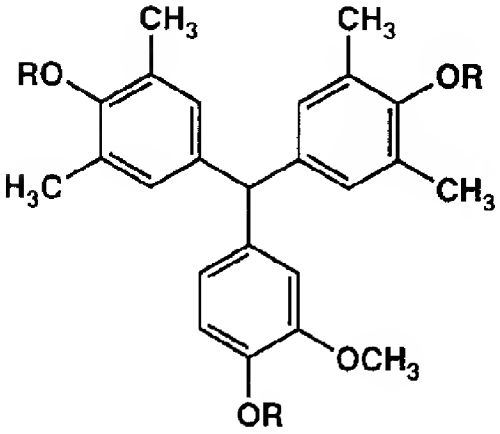

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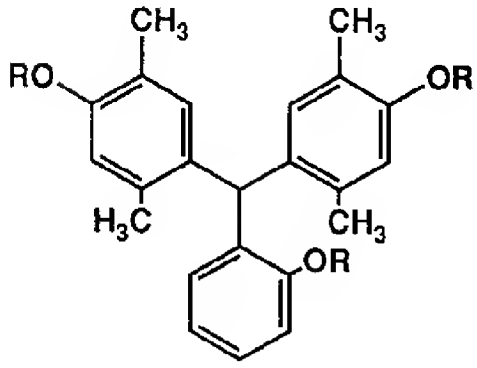
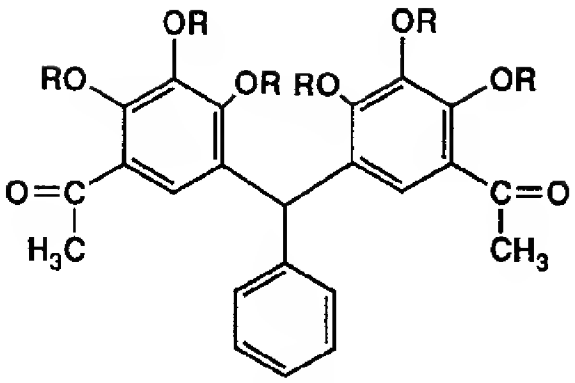


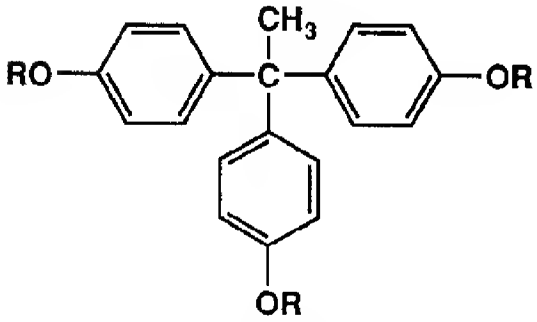
(13)

[0044]

[Formula 18]



(14)



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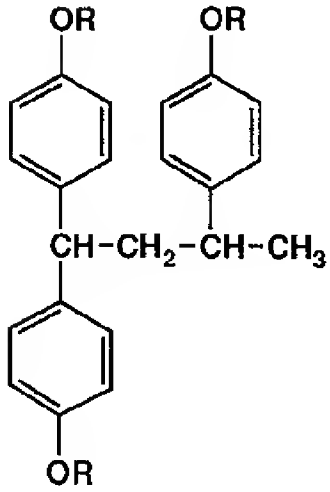
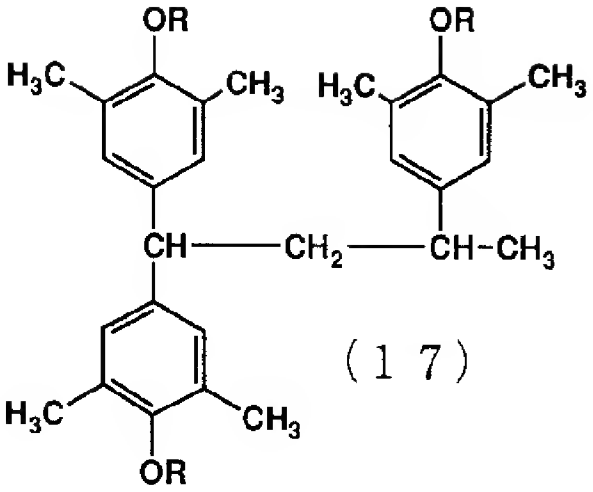


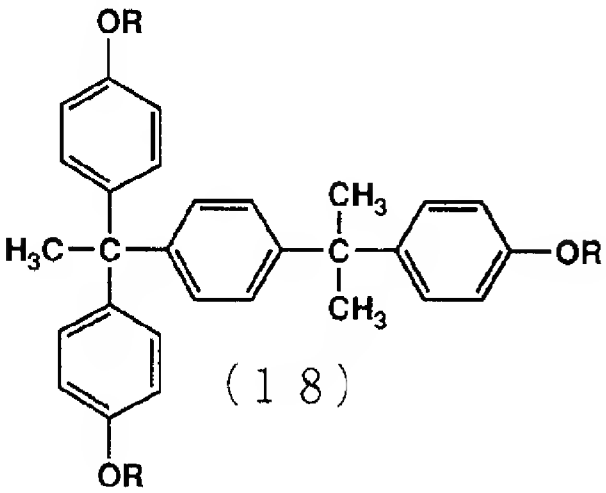
(16)

[0045]

[Formula 19]



(17)



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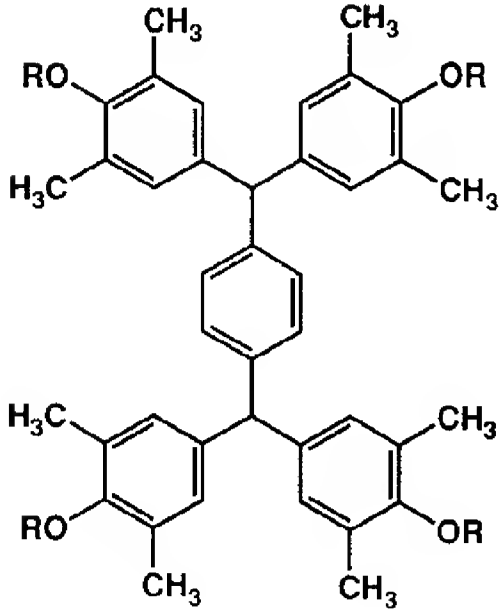
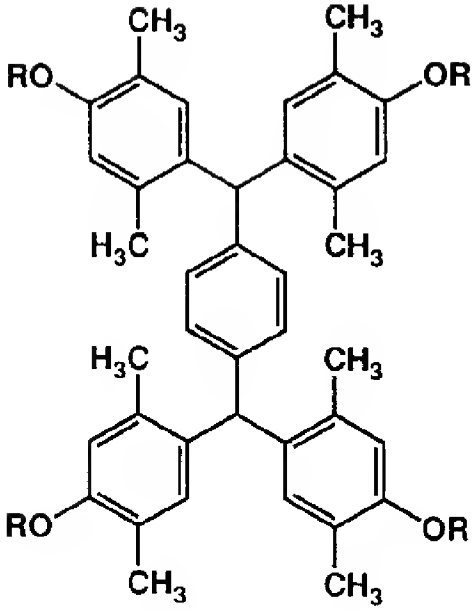


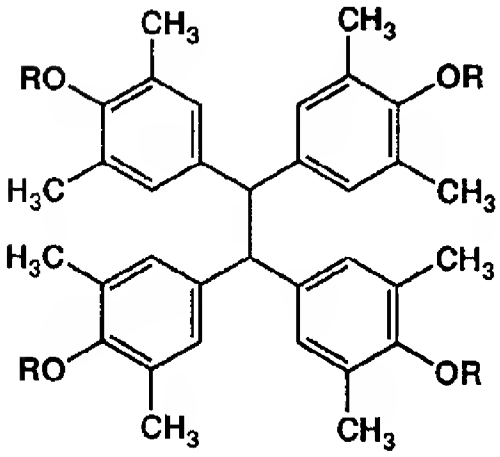
(19)

[0046]

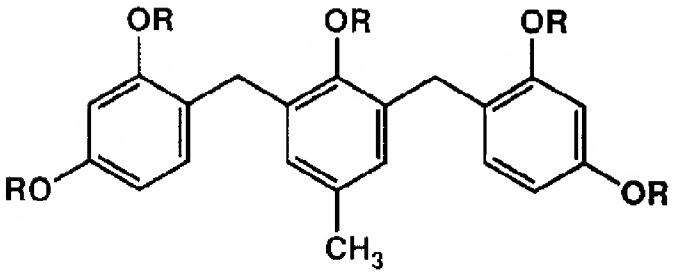
[Formula 20]



(20)



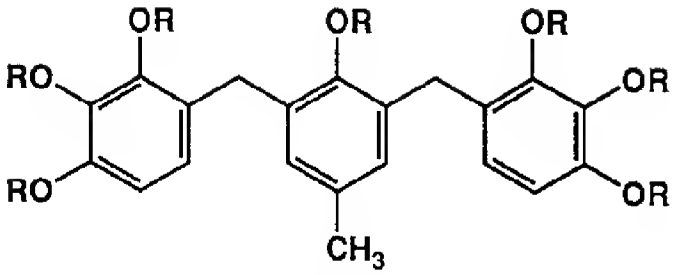
(21)



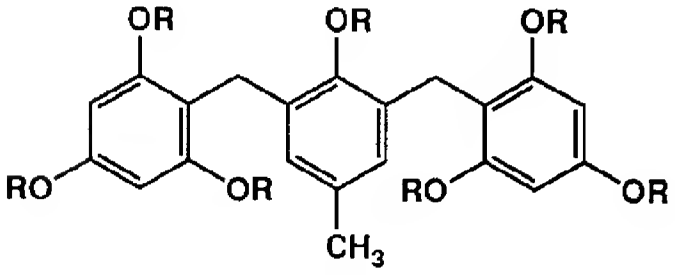
(22)

[0047]

[Formula 21]



(23)



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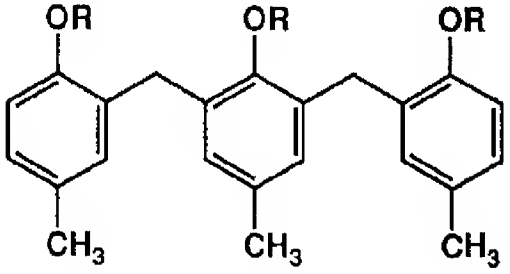

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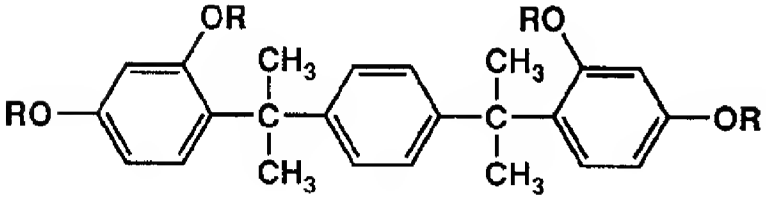
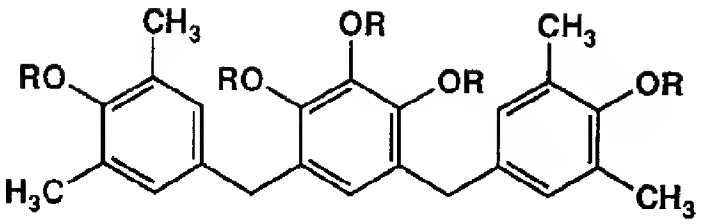


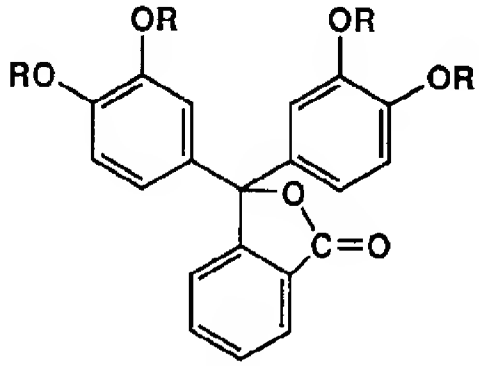
(26)

[0048]

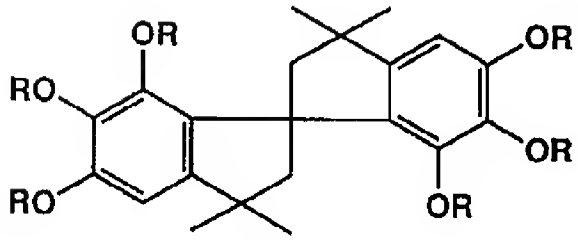
[Formula 22]



(27)



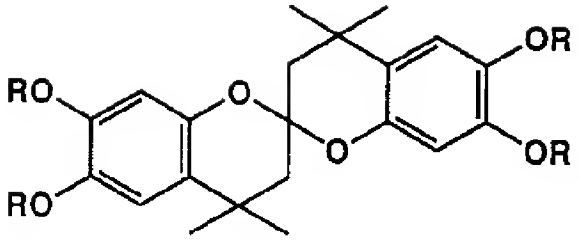
(28)



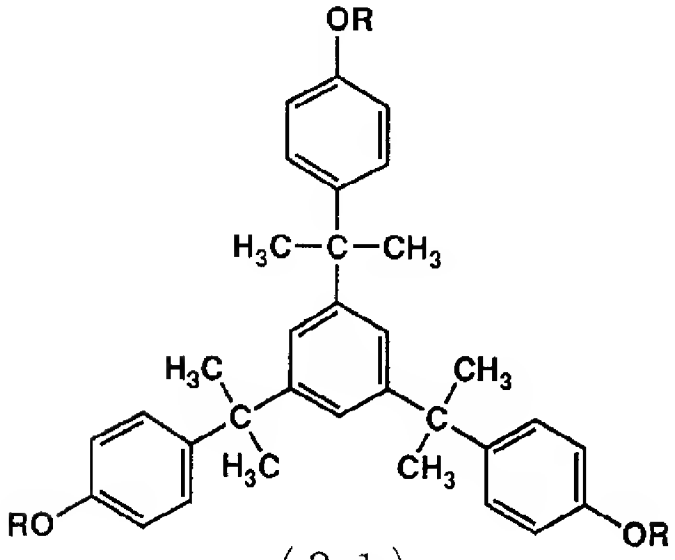
(29)

[0049]

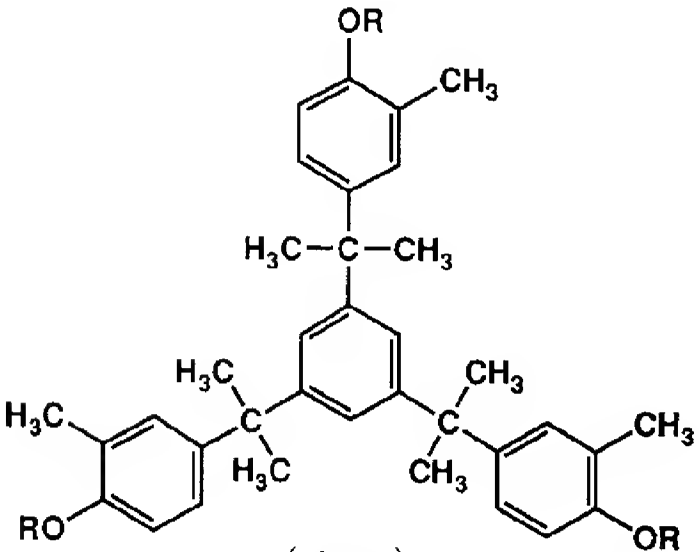
[Formula 23]



(30)



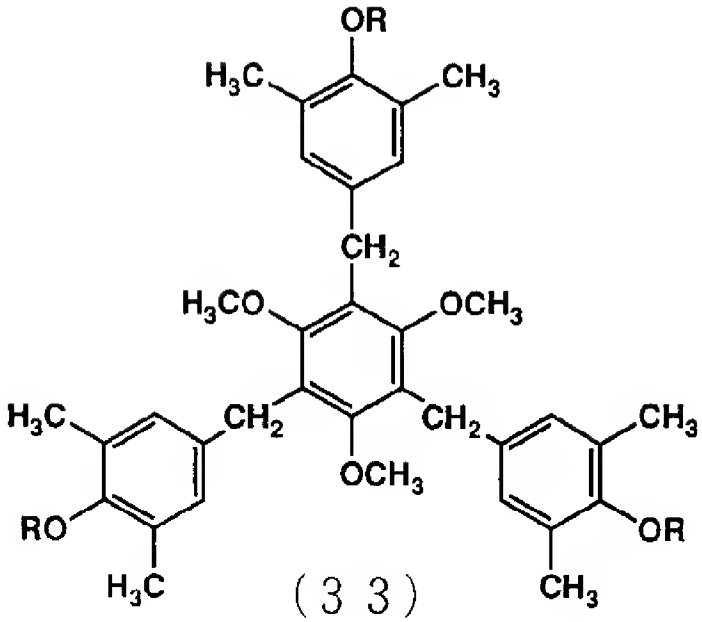
(31)



(32)

[0050]

[Formula 24]



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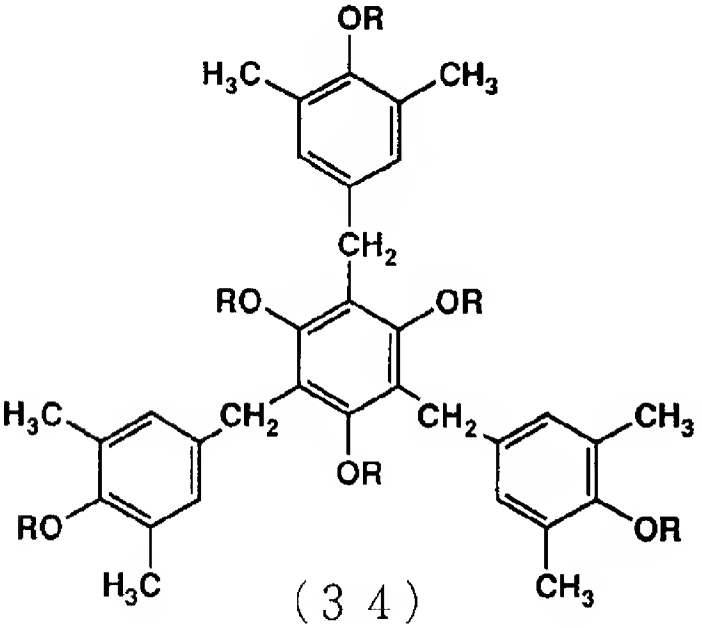
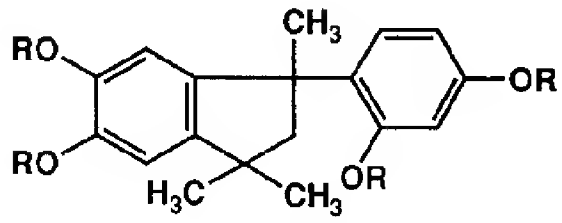


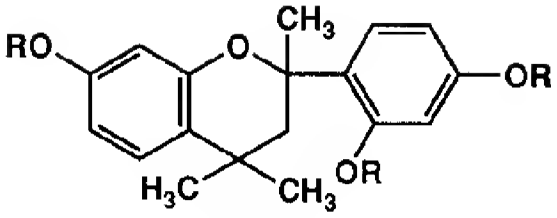
(34)



(35)

[0051]

[Formula 25]



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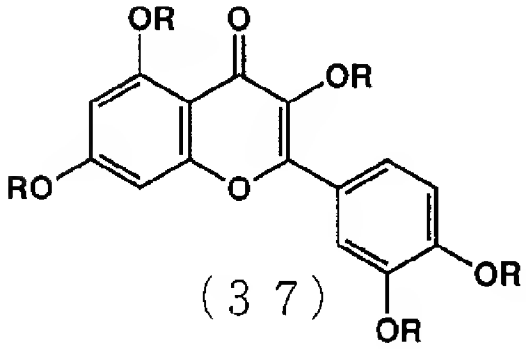
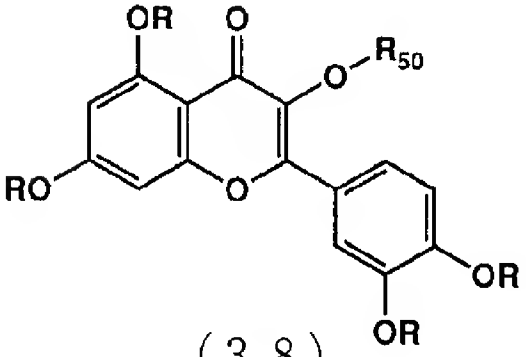
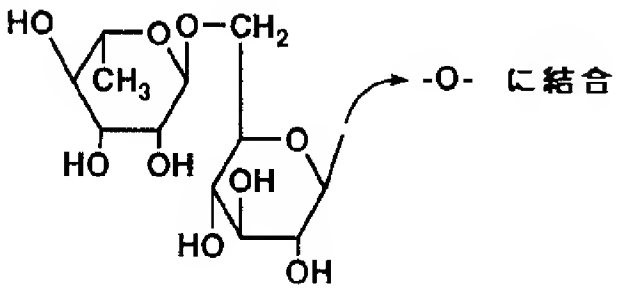


(37)



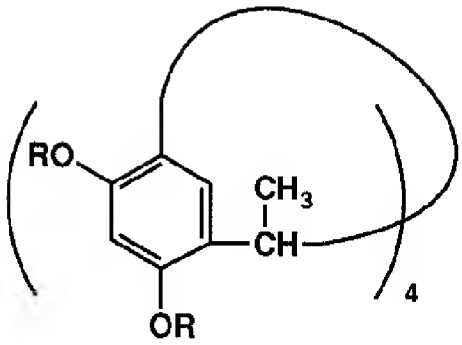
(38)

但し、R_{50}:

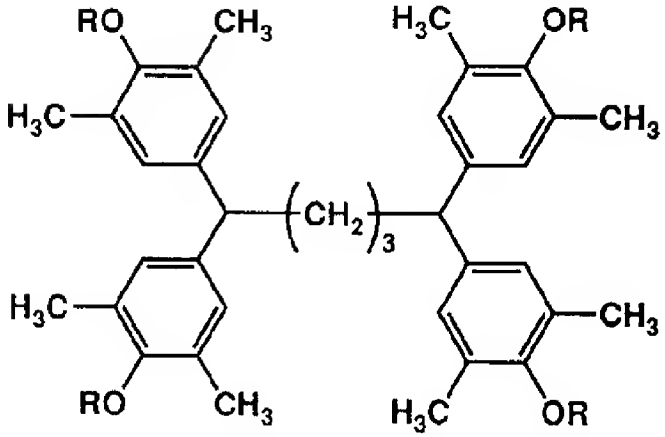


[0052]

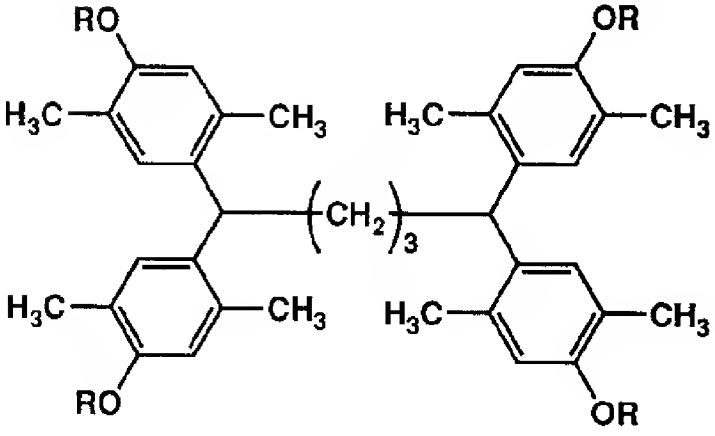
[Formula 26]



(39)



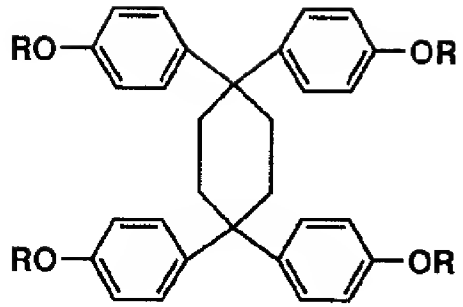
(40)



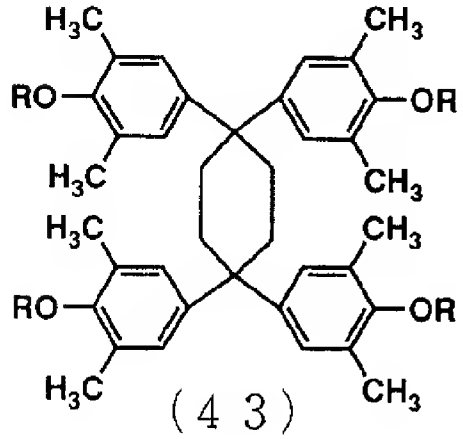
(41)

[0053]

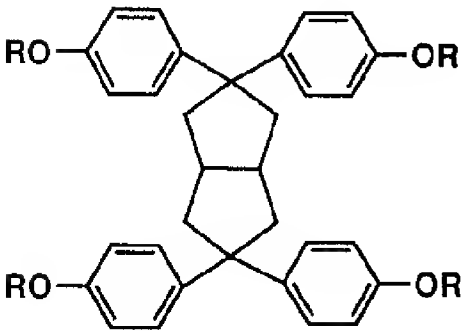
[Formula 27]



(42)



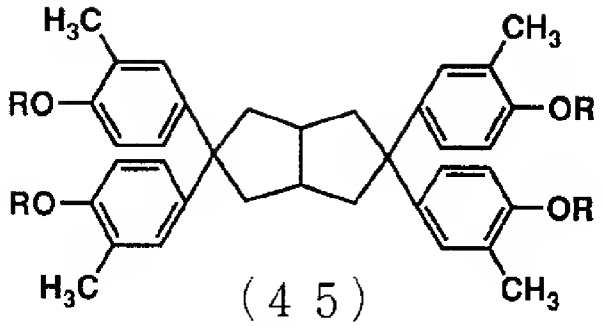
(43)



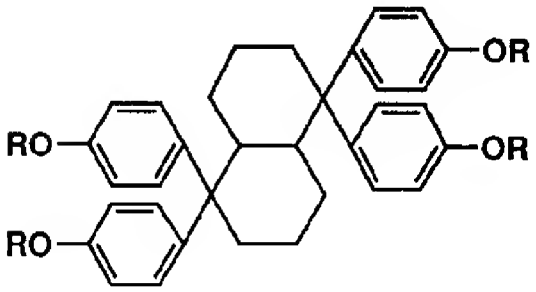
(44)

[0054]

[Formula 28]



(45)



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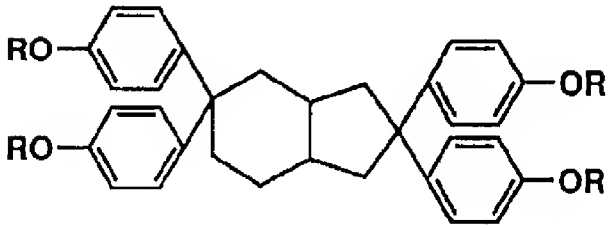
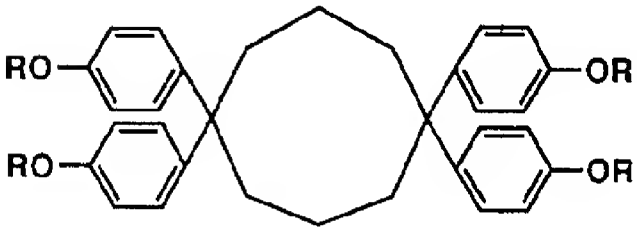


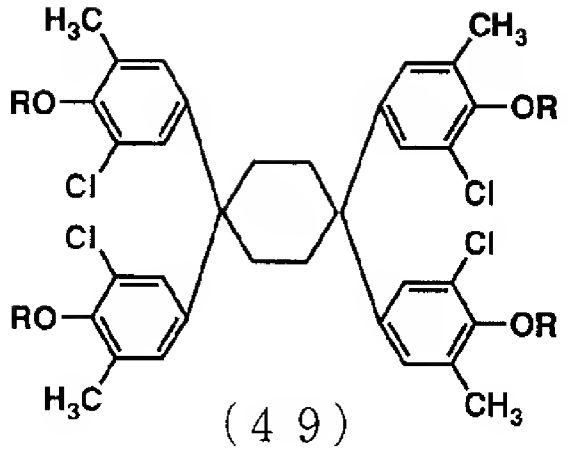
(47)



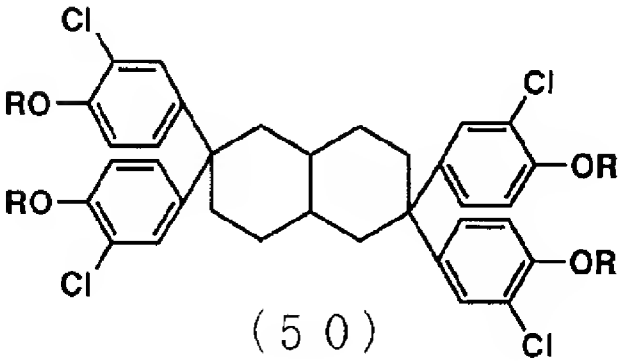
(48)

[0055]

[Formula 29]



(49)



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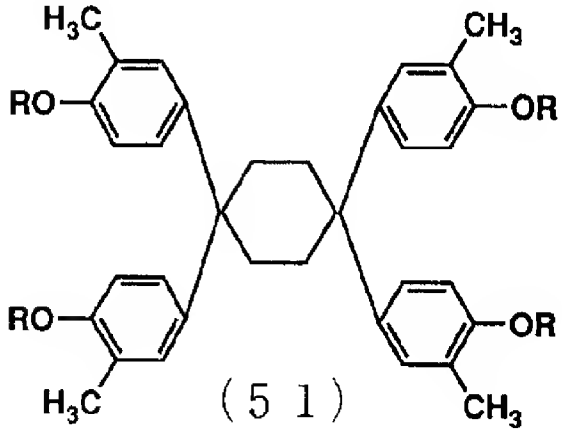
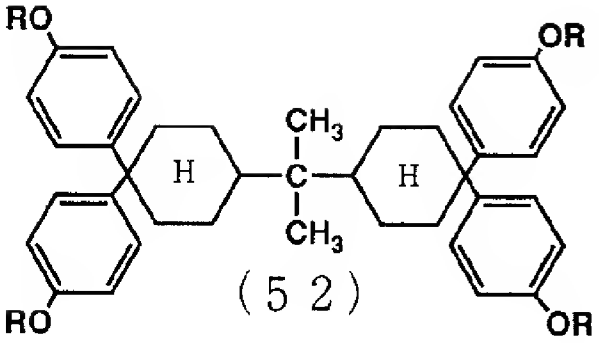


(51)

[0056]

[Formula 30]



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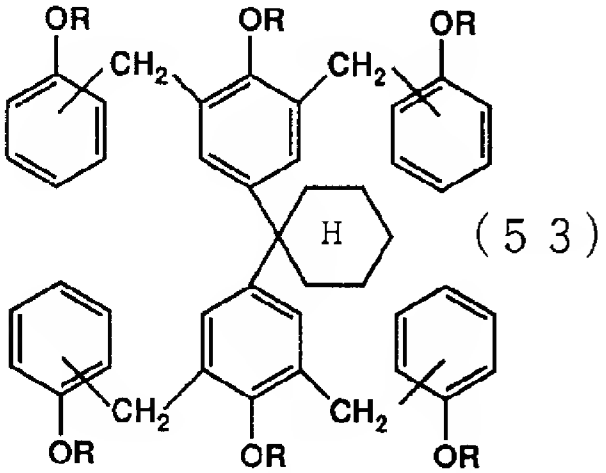

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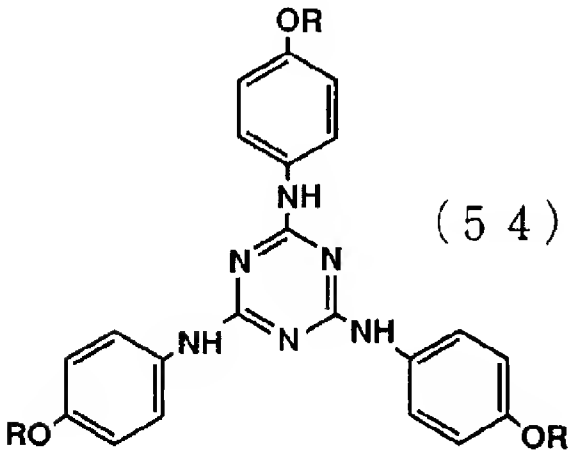

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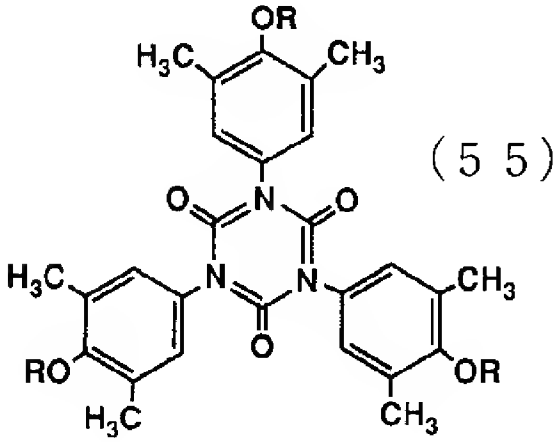
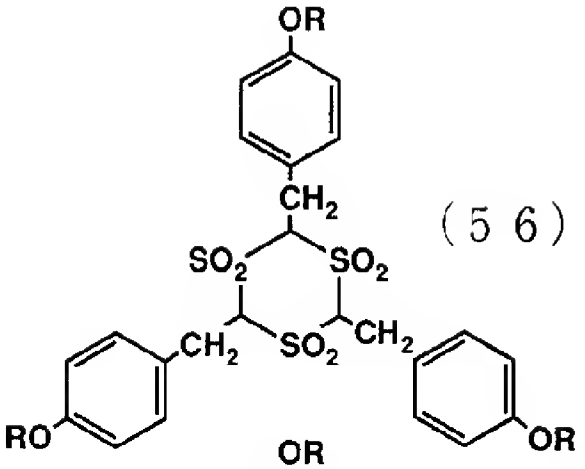


(55)

[0057]

[Formula 31]



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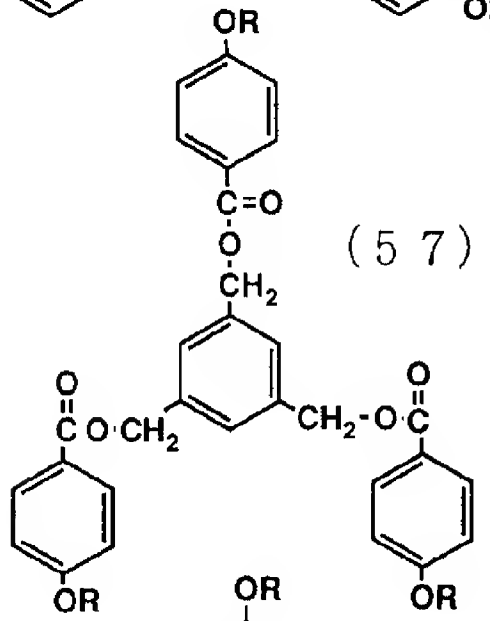

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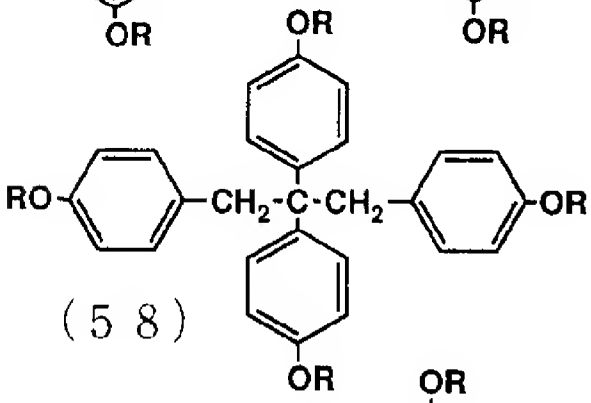
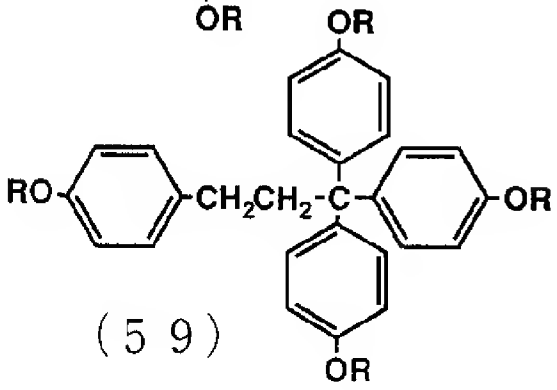


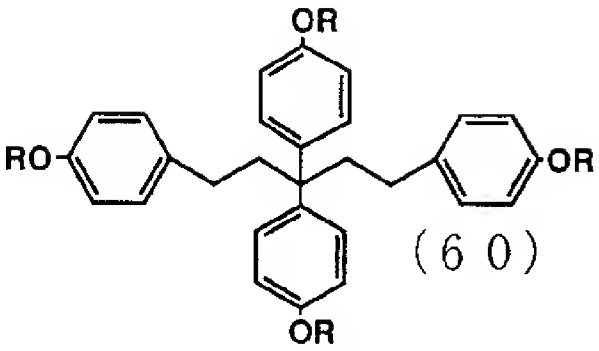
(58)



(59)

[0058]

[Formula 32]



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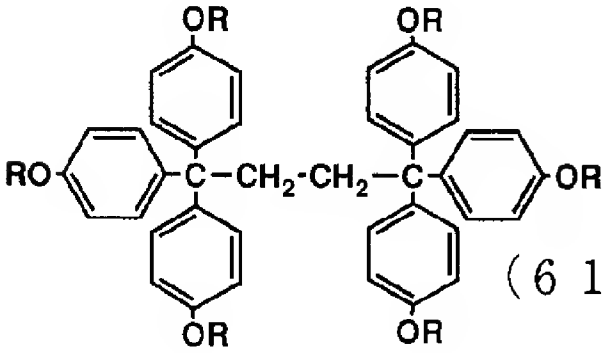
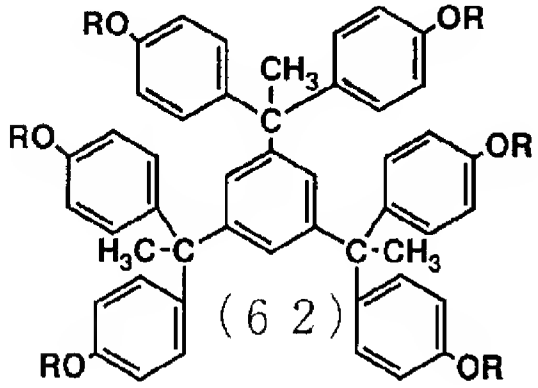
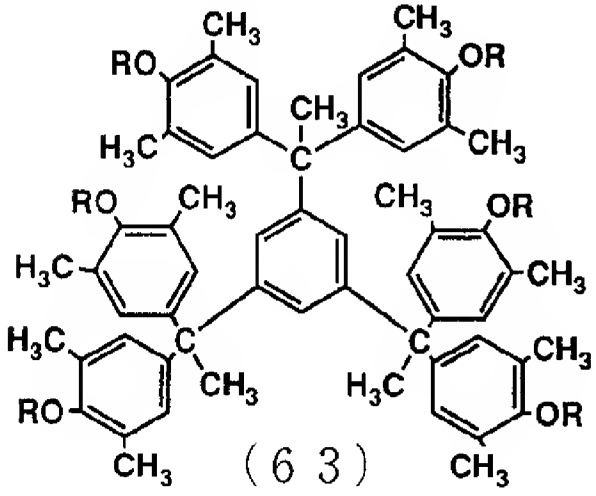


(61)



(62)



(63)

[0059]R in compound (1) – (63) is a hydrogen atom, [0060]

[Formula 33]

$-CH_2-COO-C(CH_3)_2C_6H_5$、$-CH_2-COO-C_4H_9^t$、
$-COO-C_4H_9^t$もしくは 

[0061]******. However, three pieces may be bases other than a hydrogen atom by at least two pieces or structure, and each substituent R may not be the same basis.

[0062]An addition of a compound used for this invention (c) is 3 to 50 % of the weight on the basis of full weight (except for a solvent) of a photosensitive composition, and is 5 to 35% of the weight of a range preferably.

[0063](B) Solvent (compound of this invention (d))

Solvents which may dissolve each ingredient of (a) – (c) of this invention used for this invention (d) are a range whose boiling point is 130–155 **, and a solvent which is in the range of 140–155 ** preferably. In 30 to 100 % of the weight of all the solvent Naka, the content is preferably used in 70 to 100% of the weight of the range still more preferably 50 to 100% of the weight. When there are many contents of a solvent in which the boiling point exceeds 155 **, residual solvent volume after spreading / desiccation and in this film increases a photosensitive composition of this invention on a substrate. As a result, the diffusibility of acid by which it was generated at the time of pattern exposure becomes large, and shape of a pattern to form deteriorates. On the other hand, when the boiling point is a solvent below 130 **, the compatibility of a photosensitive composition of this invention deteriorates and sensitivity falls. Therefore, only when using a solvent which has the boiling point for a mentioned range in quantity of a mentioned range, a good profile, sensitivity, and resolution are attained.

[0064]The boiling point as a solvent which is 130–155 ** specifically, N–amyl acetate, isoamyl acetate, propionic acid n–butyl, 3–methoxy methyl propionate, Butanoic acid n–propyl, methyl lactate, ethyl lactate, ethyl pyruvate, alpha–hydroxy isobutyric acid methyl, Although ethylene glycol monomethyl ether acetate, propylene–glycol–monomethyl–ether acetate, 2–heptanone, 3–heptanone, 4–heptanone, 4–ethoxy–2–butanone, an acetylacetone, 2–ethoxyethanol, etc. are mentioned, It is not limited to this. These solvents can be used within the limits of previous statement, being able to be independent or mixing. As a solvent which can be mixed, ethylene dichloride, cyclohexanone, 2–butanone, gamma–butyllactone, 2–methoxyethanol, 1–methoxy–2–propanol, 1–methoxy–2–butanol, 3–methoxybutanol, 3–methyl–3–methoxybutanol, Diacetone alcohol, diethylene glycol dimethyl ether, diethylene–glycol–monomethyl–ether acetate, Dimethoxyethane, 3–methoxy butyl acetate, ethylene glycol monoethyl ether acetate, 3–ethoxyethyl propionate, 4–n–propoxy–2–butanone, 4–isobutoxy–2–butanone, 2–methoxy–2–methyl–4–pentanone, Acetoxy 2–propanone, methyl acetoacetate, alpha–hydroxy isobutyric acid ethyl, Ethyl acetate, toluene, a tetrahydrofuran, dioxane, N.N–dimethylformamide, N,N–dimethylacetamide, dimethyl sulfoxide, N–methyl pyrrolidone, tetramethyl urea, etc. are mentioned.

[0065]

(C) Alkalis soluble resin (compound of this invention (a))

As alkalis soluble resin used for this invention, For example, novolak resin, hydrogenation novolak resin, acetone pyrogallol resin, Polyhydroxy styrene, halogen, or alkylation polyhydroxy styrene, a part of

hydroxystyrene N-substitution maleimide copolymer and polyhydroxy styrene, although O-alkylation thing or O-acylation thing, a styrene maleic anhydride copolymer, carboxyl group content methacrylic system resin, and its derivative can be mentioned, It is not limited to these. Especially desirable alkalis soluble resin is novolak resin and polyhydroxy styrene. This novolak resin is obtained by carrying out addition condensation to aldehyde under existence of an acid catalyst by using a predetermined monomer as the main ingredients.

[0066]As a predetermined monomer, phenol, m-cresol, p-cresol, Cresol, such as o-cresol, a 2,5-xylenol, 3,5-xylenol, Xylenols, such as a 3,4-xylenol and a 2,3-xylenol. m-ethylphenol, p-ethylphenol, o-ethylphenol, Alkylphenols, such as p-t-butylphenol, p-octyl phenol, and 2,3,5-trimethyl phenol. p-methoxy phenol, m-methoxy phenol, 3,5-dimethoxyphenol, 2-methoxy-4-methyl phenol, m-ethoxyphenol, p-ethoxyphenol, m-propoxyphenol, p-propoxyphenol, m-butoxyphenol, Screw alkylphenols, such as alkoxy phenols, such as p-butoxyphenol, and 2-methyl-4-isopropyl phenols. hydroxy aroma compounds, such as m-chlorophenol, p-chlorophenol, o-chlorophenol, dihydroxybiphenyl, bisphenol A, phenylphenol, resorcinol, and naphthol,, although two or more kinds can use it, being able to be independent or mixing, It is not limited to these.

[0067]As aldehyde, for example Formaldehyde, paraformaldehyde, Acetaldehyde, propylaldehyde, benzaldehyde, phenylacetaldehyde, alpha-phenylpropyl aldehyde, beta-phenylpropyl aldehyde, O-hydroxybenzaldehyde, m-hydroxybenzaldehyde, p-hydroxybenzaldehyde, o-chlorobenzaldehyde, m-chlorobenzaldehyde, p-chlorobenzaldehyde, o-nitrobenzaldehyde, m-nitrobenzaldehyde, p-nitrobenzaldehyde, o-methylbenzaldehyde, m-methylbenzaldehyde, Although p-methylbenzaldehyde, p-ethylbenzaldehyde, p-n-butylbenzaldehyde, furfural, chloroacetaldehyde, and these acetal objects, for example, a chloroacetaldehyde diethyl acetal etc., can be used, In these, it is preferred to use formaldehyde. Such aldehyde is independent, or they are combined two or more kinds and used. As an acid catalyst, chloride, sulfuric acid, formic acid, acetic acid, oxalic acid, etc. can be used.

[0068]In this way, as for weight average molecular weight of obtained novolak resin, it is preferred that it is the range of 1,000-30,000. By less than 1,000, film decrease after development of an unexposed part is large, and if 30,000 is exceeded, developing velocity will become small. Ranges especially of a suitable thing are 2,000-20,000. Here, weight average molecular weight has a polystyrene reduced property of gel permeation chromatography, and is defined.

[0069]Two or more kinds may use these alkalis soluble resin in this invention, mixing. The amount of alkalis soluble resin used is 60 to 90 % of the weight preferably 50 to 97% of the weight on the basis of full weight (except for a solvent) of a photosensitive composition.

[0070](D) A compound which generates acid by the exposure of active light or radiation (compound of this invention (b))

As a compound which decomposes by the exposure of active light or radiation used by this invention, and generates acid, Compounds which generate acid by a publicly known light currently used for a photoinitiator of optical cationic polymerization, a photoinitiator of an optical radical polymerization, an optical decolorizing agent of coloring matter, optical alterant, or micro resist, and those mixtures can be used choosing them suitably. For example, S.I.Schlesinger, Photogr.Sci.Eng., 18,387 (1974), T.S. Diazonium salt given in Bal etal, Polymer, 21,423 (1980), etc., U.S. Pat. No. 4,069,055 and said 4,069,056 No. -- said -- Re No. 27,992, Ammonium salt given in Japanese Patent Application No. No. 140,140 [three to] etc., D.C.Necker etal,

Macromolecules, 17, 2468 (1984), C.S. Wen etal, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), Phosphonium salt given in U.S. Pat. No. 4,069,055, the 4,069,056 No., etc., J. V.Crivello etal, Macromorecules, 10 (6), Iodonium salt given in 1307 (1977), Chem.&Eng.News, Nov.28, p31 (1988), European patent No. 104,143, U.S. Pat. No. 339,049, 410,201, JP,2-150,848,A, JP,2-296,514,A, etc., J. V.Crivello etal, Polymer J.17, 73 (1985), J. V.Crivello etal.J.Org.Chem., 43, 3055 (1978), W.R. Watt etal, J.Polymer Sci., Polymer Chem.Ed., 22, 1789 (1984), J. V.Crivelloetal, Polymer Bull., 14,279 (1985), J. V.Crivello etal, Macromorecules, 14 (5), 1141 (1981), J.V.Crivello etal, J.PolymerSci., Polymer Chem.Ed., 17, 2877 (1979), the 370,693rd item of an European patent, and said 3,902,114 No. -- said -- No. 233,567, Said 297,443 No., said 297,442 No., U.S. Pat. No. 4,933,377, Sulfonium salt given in said 161,811 No., said 410,201 No., said 339,049 No., said 4,760,013 No., said 4,734,444 No., said 2,833,827 No., the Germany patent No. 2,904,626, said 3,604,580 No., the 3,604,581 No., etc., J. V.Crivello etal, Macromorecules, 10 (6), A seleno NIUMU salt given in 1307 (1977), J.V.Crivello etal, J.PolymerSci., Polymer Chem.Ed., 17-1047 (1979), etc., C.S. Onium salt, such as arsonium salt given in Wen etal, Teh, Proc.Conf.Rad.Curing ASIA, p478 Tokyo, Oct (1988), etc., U.S. Pat. No. 3,905,815, JP,46-4605,B, JP,48-36281,A, JP,55-32070,A, JP,60-239736,A, JP,61-169835,A, JP,61-169837,A, JP,62-58241,A, JP,62-212401,A, An organic halogenated compound given in JP,63-70243,A, JP,63-298339,A, etc., K. Meier etal, J.Rad.Curing, 13 (4), 26 (1986), T.P.Gill etal, Inorg.Chem., 19 and 3007 (1980), D.Astruc, Acc.Chem.Res., 19 (12), 377 (1896), An organic metal/organic halogenated compound given in JP,2-161445,A etc., S. Hayase etal, J.Polymer Sci., 25,753 (1987),E. Reichmanis etal, J.Pholymer Sci., Polymer Chem.Ed., 23, 1 (1985),Q.Q. Zhu etal, J.Photochem., 36, 85, 39,317 (1987),B. Amit etal, Tetrahedron Lett., (24) 2205 (1973),D.H.R. Barton etal, J.Chem Soc., 3571 (1965),P.M. Collins etal, J.Chem.SoC., Perkin I, 1695 (1975),M. Rudinstein etal, Tetrahedron Lett., (17), 1445 (1975), J.W.Walker etalJ.Am.Chem.Soc., 110 and 7170 (1988), S.C.Busman etal, J.Imaging Technol., 11 (4), 191 (1985),H.M. Houlihan etal, Macormolecules, 21, 2001 (1988),P.M. Collins etal, J.Chem.Soc., Chem.Commun., 532 (1972),S. Hayase etal, Macromolecules, 18, 1799 (1985),E. Reichmanis etal, J.Electrochem.Soc., Solid State Sci.Technol., 130 (6), F.M. Houlihan etal, Macromolcules, 21, 2001 (1988),European patent 0290th and No. 750 -- said -- No. 046 or 083 -- said -- No. 156 or 535, Said 271,851 No., said 0,388,343 No., U.S. Pat. No. 3,901,710, A photo-oxide generating agent which has 0-nitrobenzyl type protective group of a statement in said 4,181,531 No., JP,60-198538,A, JP,53-133022,A, etc., M. TUNOOKA etal, Polymer Preprints Japan, 35 (8), G.Berner etal, J.Rad.Curing, 13 (4), W.J. Mijs etal, Coating Technol., 55 (697), 45 (1983), Akzo, H.Adachi etal, Polymer Preprints, Japan, 37 (3), European patent 0199th, No. 672, and said 84515 No. -- said -- No. 199 or 672, said -- No. 044 or 115 -- said -- No. 0101 or 122 and U.S. Pat. No. 4,618,564. Said 4,371,605 No., said 4,431,774 No., JP,64-18143,A, It is an account to a compound which carries out a photolysis and generates sulfonic acid, JP,61-166544,A, etc. which are represented by imino sulfonate given in JP,2-245756,A, Japanese Patent Application No. No. 140109 [three to], etc. A disulfon compound of ** can be mentioned. [0071]a basis which generates acid by such lights or a compound -- a main chain of polymer -- or -- a compound introduced into a side chain. For example, M.E.Woodhouse etal, J.Am.Chem.Soc., 104, 5586 (1982), S.P. Pappas etal, J.Imaging Sci., 30 (5), 218 (1986), S.Kondoetal, Makromol.Chem., Rapid Commun., 9,625 (1988), Y. Yamadaetal, Makromol.Chem., 152,153,163 (1972), J. V.Crivello etal, J.PolymerSci., Polymer Chem.Ed., 17, 3845 (1979), U.S. Pat. No. 3,849,137, the 3914407th JP,63-26653,A of the Germany patent, JP,55-164824,A, JP,62-69263,A, JP,63-146038,A A compound of a statement can be used for

JP,63-163452,A, JP,62-153853,A, JP,63-146029,A, etc.

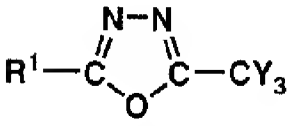
[0072]Furthermore, V.N.R.Pillai, Synthesis, (1), 1 (1980), A. Abad etal, Tetrahedron Lett., (47) 4555 (1971), D.H.R. A compound which generates acid by light of a statement can also be used for Barton etal, J.Chem.Soc., (C), 329 (1970), U.S. Pat. No. 3,779,778, European patent No. 126,712, etc.

[0073]In a compound which decomposes by the exposure of the above-mentioned active light or radiation, and generates acid, especially a thing used effectively is explained below.

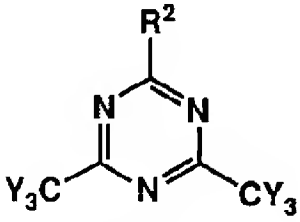
(1) S-triazine derivative expressed with an oxazole derivative or a general formula (PAG2) expressed with a following general formula (PAG1) which a trihalomethyl group replaced.

[0074]

[Formula 34]



(PAG1)

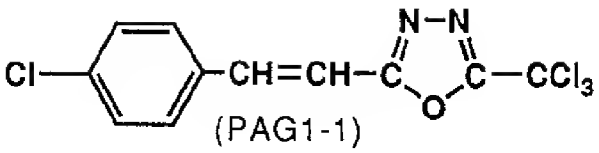


(PAG2)

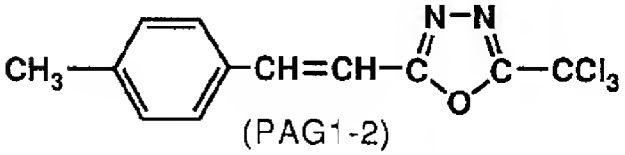
[0075]As for R^1, the aryl group which is not replaced [substitution or], an alkenyl group, and R^2 show among a formula the aryl group which is not replaced [substitution or], an alkenyl group, an alkyl group, and $-CY_3$. Y ********** or a bromine atom is shown. Although the following compounds can specifically be mentioned, it is not limited to these.

[0076]

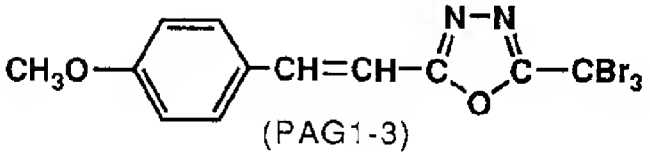
[Formula 35]



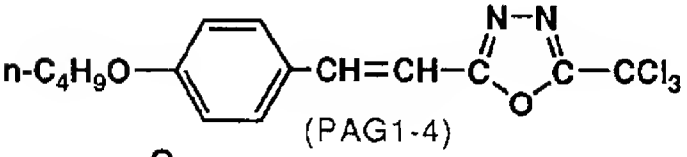
(PAG1-1)



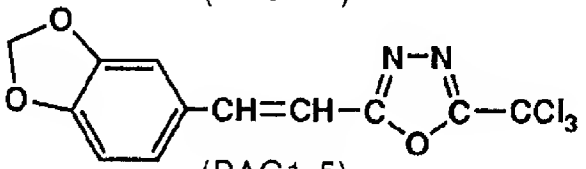
(PAG1-2)



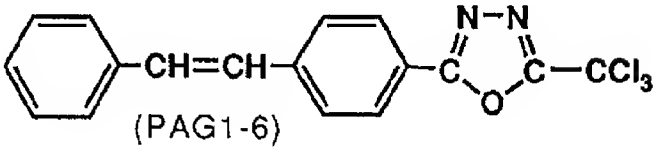
(PAG1-3)



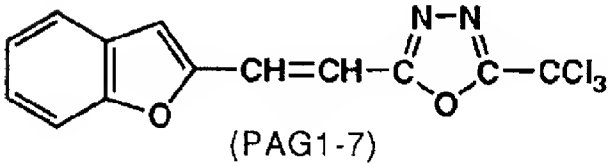
(PAG1-4)



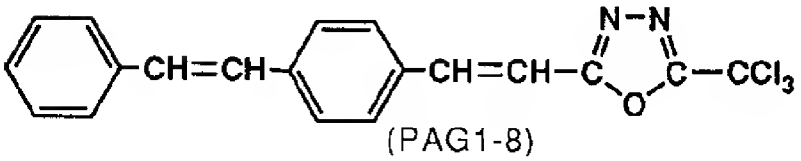
(PAG1-5)



(PAG1-6)



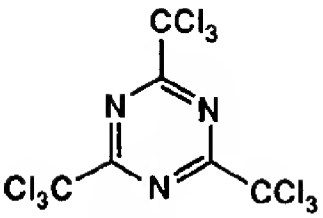
(PAG1-7)



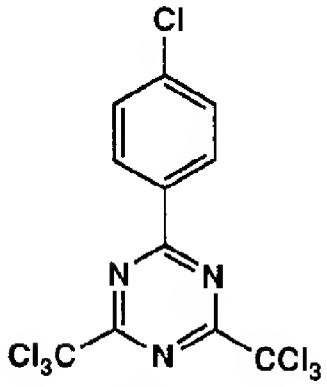
(PAG1-8)

[0077]

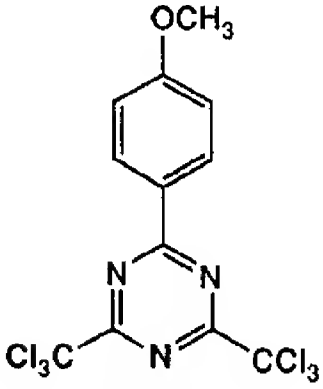
[Formula 36]



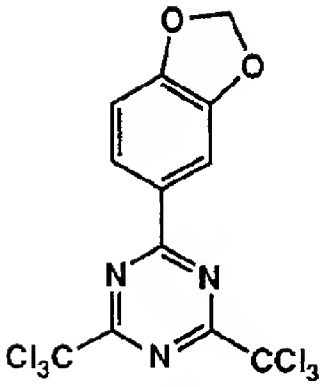
(PAG2-1)



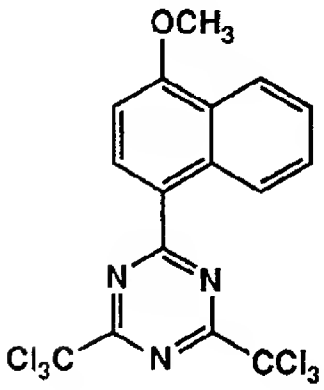
(PAG2-2)



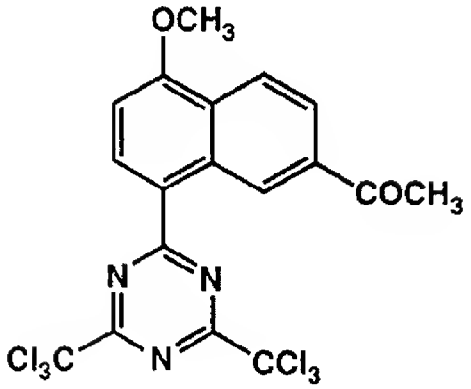
(PAG2-3)



(PAG2-4)



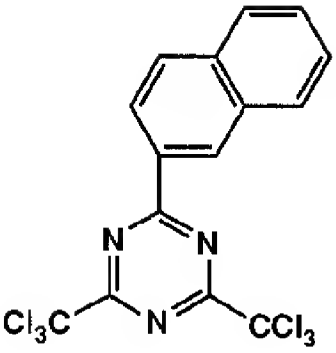
(PAG2-5)



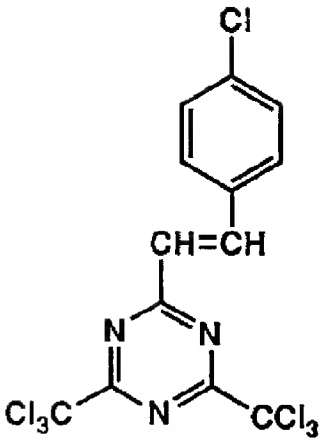
(PAG2-6)

[0078]

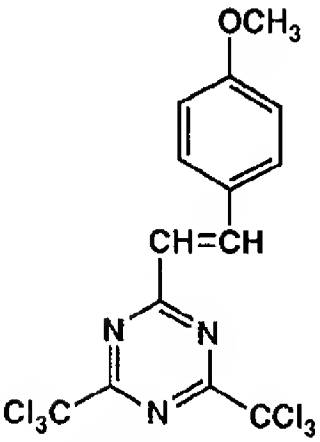
[Formula 37]



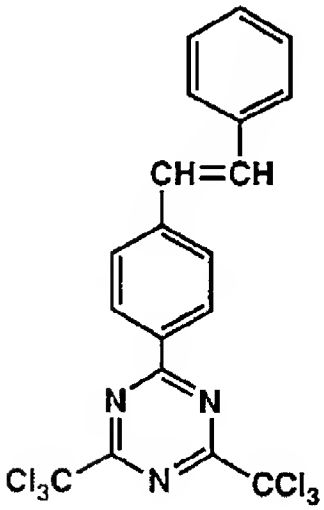
(PAG2-7)



(PAG2-9)



(PAG2-8)

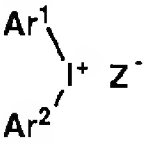


(PAG2-10)

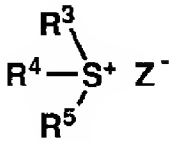
[0079](2) Iodonium salt expressed with the following general formula (PAG3), or sulfonium salt expressed with a general formula (PAG4).

[0080]

[Formula 38]



(PAG3)



(PAG4)

[0081]Formula Ar^1 and Ar^2 show respectively the aryl group which is not replaced [substitution or] independently here. As a desirable substituent, an alkyl group, a halo alkyl group, a cycloalkyl group, an aryl group, an alkoxy group, a nitro group, a carboxyl group, an alkoxycarbonyl group, a HIRODOKISHI group, a sulfhydryl group, and a halogen atom are mentioned.

[0082]R^3, R^4, and R^5 show respectively an alkyl group which is not replaced [substitution or] and an aryl group independently. They are an aryl group of the carbon numbers 6-14, alkyl groups of the carbon

numbers 1–8, and those substituted derivatives preferably. As a desirable substituent, to an aryl group, an alkoxy group of the carbon numbers 1–8, It is an alkyl group, a nitro group, a carboxyl group, a HIRODOKISHI group, and a halogen atom of the carbon numbers 1–8, and they are an alkoxy group of the carbon numbers 1–8, a carboxyl group, and an ARUKOSHIKI carbonyl group to an alkyl group.

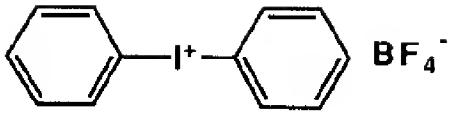
[0083]Z^- is shown and an opposite anion For example, BF_4^-, AsF_6^-, PF_6^-, SbF_6^-, Perfluoro alkane–sulfonic–acid anions, such as SiF_6^{2-}, ClO_4^-, and $CF_3SO_3^-$, A pentafluoro benzenesulfonic acid anion, naphthalene–1–sulfo Although condensation polynuclear aromatic–sulfonic–acid anions, such as a N acid anion, an anthraquinone sulfonate anion, a sulfonic group content color, etc. can be mentioned, it is not limited to these.

[0084]Two and Ar^1 of R^3, R^4, and the R^5, and Ar^2 may be combined via each single bond or substituent.

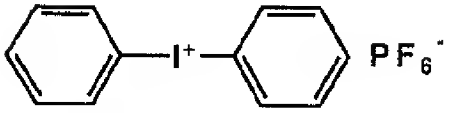
[0085]Although a compound shown below as an example is mentioned, it is not limited to these.

[0086]

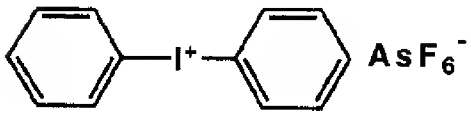
[Formula 39]



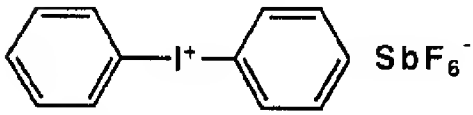
(PAG3-1)



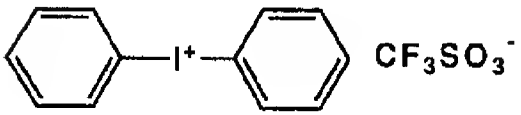
(PAG3-2)



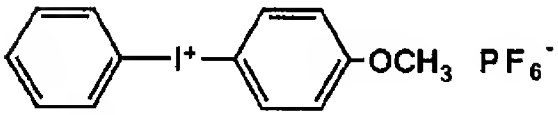
(PAG3-3)



(PAG3-4)



(PAG3-5)

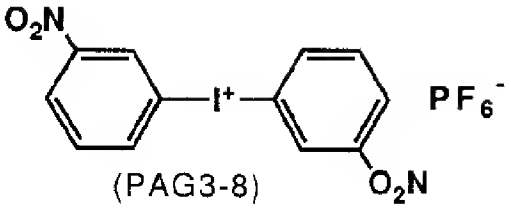


(PAG3-6)

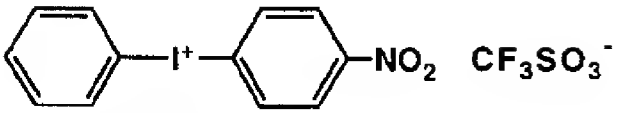
(PAG3-7)

[0087]

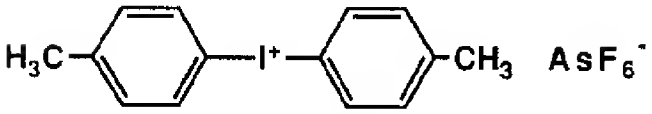
[Formula 40]



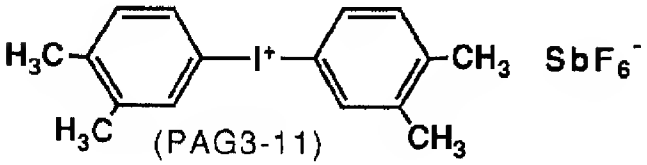
(PAG3-8)



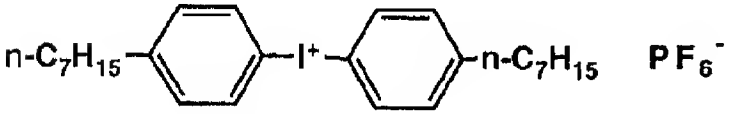
(PAG3-9)



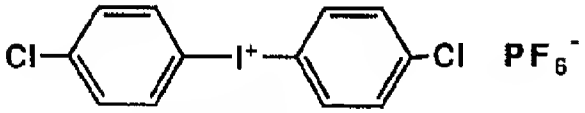
(PAG3-10)



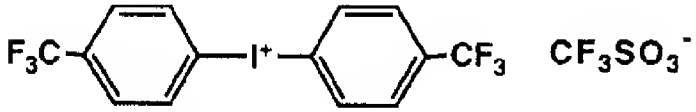
(PAG3-11)



(PAG3-12)



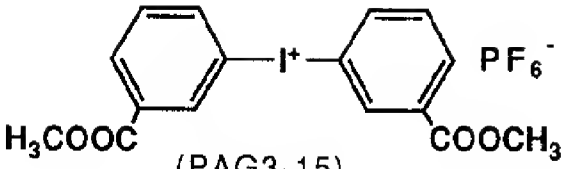
(PAG3-13)



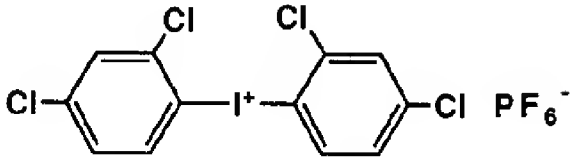
(PAG3-14)

[0088]

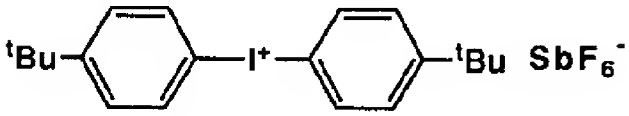
[Formula 41]



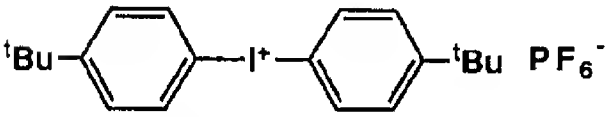
(PAG3-15)



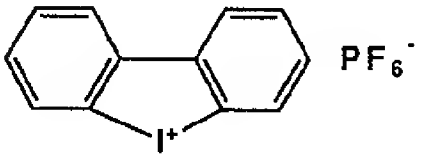
(PAG3-16)



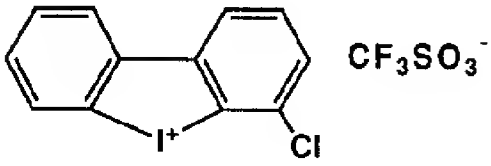
(PAG3-17)



(PAG3-18)



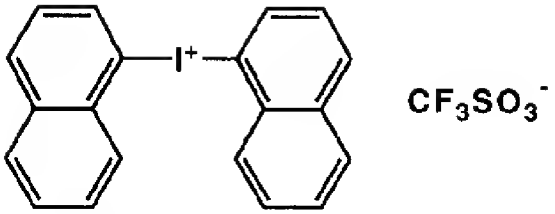
(PAG3-19)



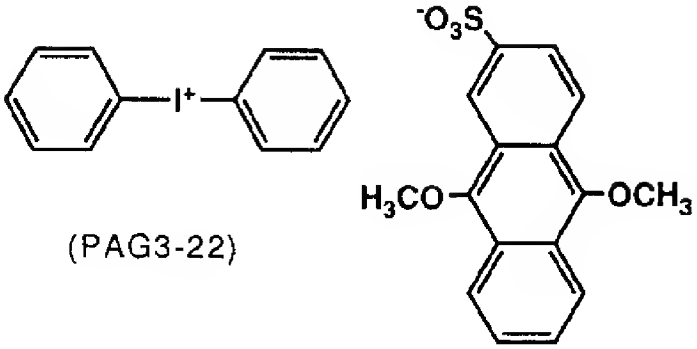
(PAG3-20)

[0089]

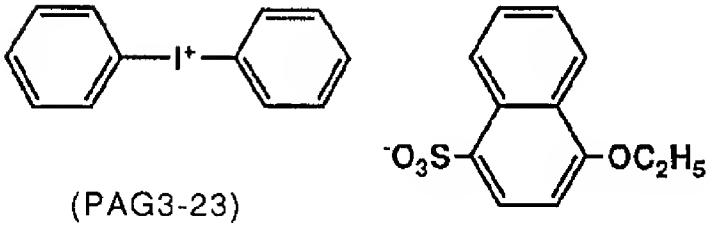
[Formula 42]



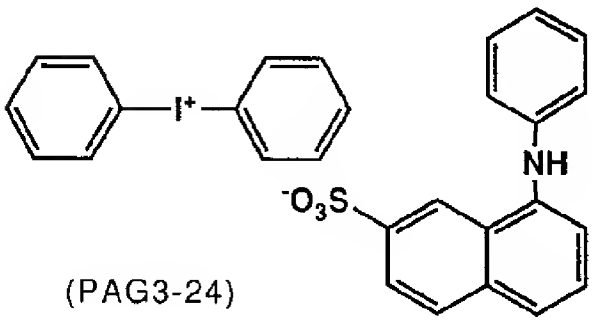
(PAG3-21)



(PAG3-22)



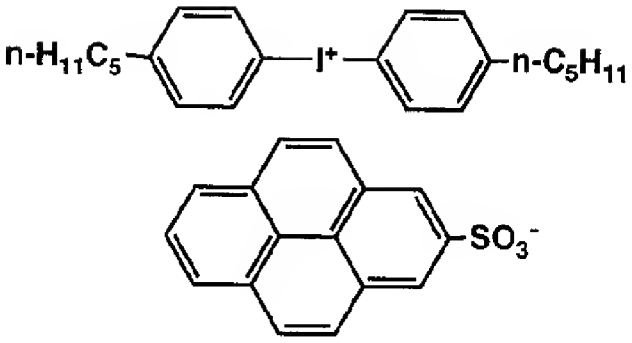
(PAG3-23)



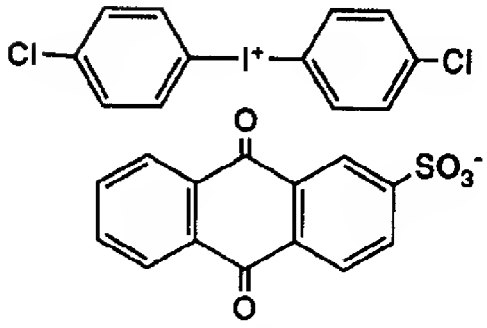
(PAG3-24)

[0090]

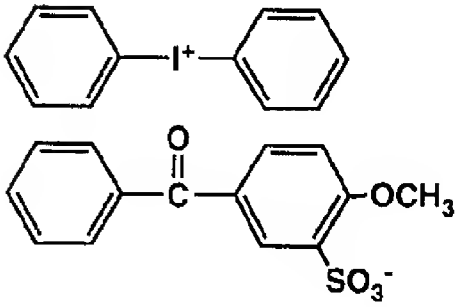
[Formula 43]



(PAG3-25)



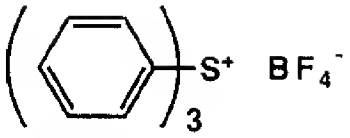
(PAG3-26)



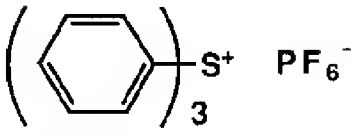
(PAG3-27)

[0091]

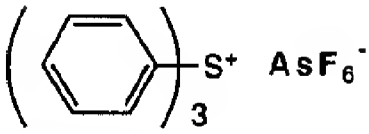
[Formula 44]



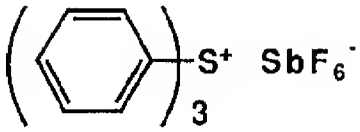
(PAG4-1)



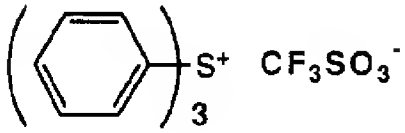
(PAG4-2)



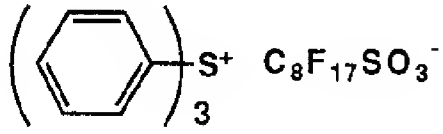
(PAG4-3)



(PAG4-4)



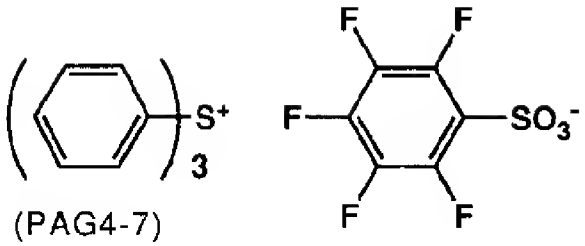
(PAG4-5)



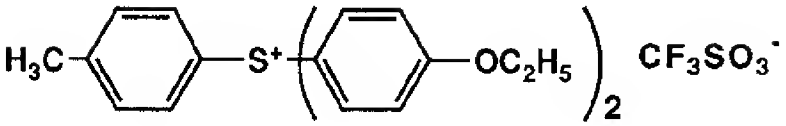
(PAG4-6)

[0092]

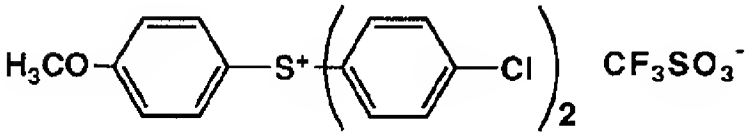
[Formula 45]



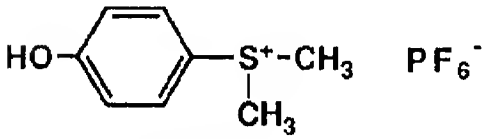
(PAG4-7)



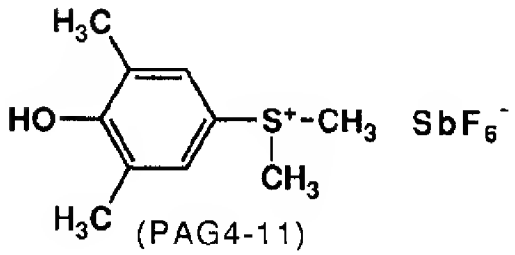
(PAG4-8)



(PAG4-9)



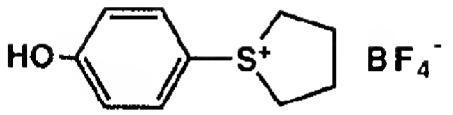
(PAG4-10)



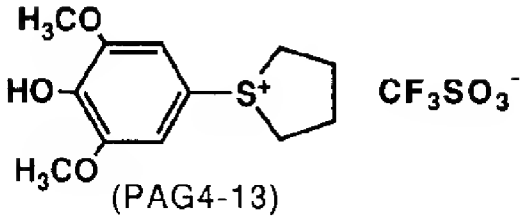
(PAG4-11)

[0093]

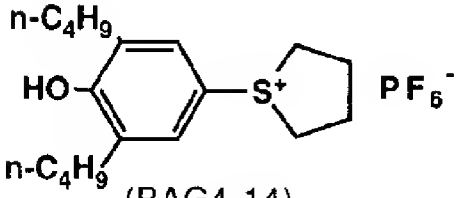
[Formula 46]



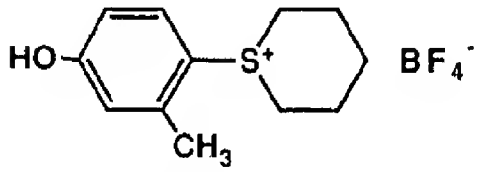
(PAG4-12)



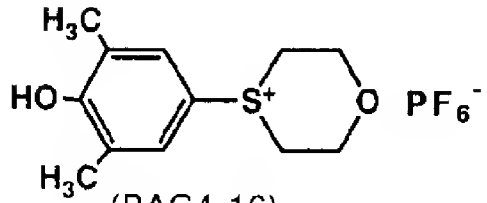
(PAG4-13)



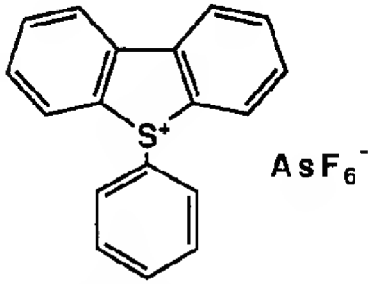
(PAG4-14)



(PAG4-15)



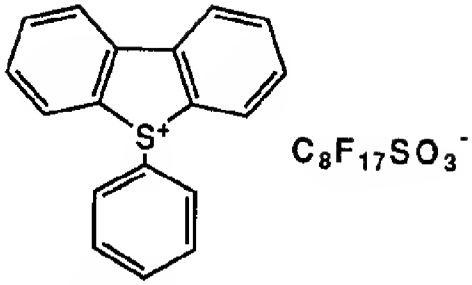
(PAG4-16)



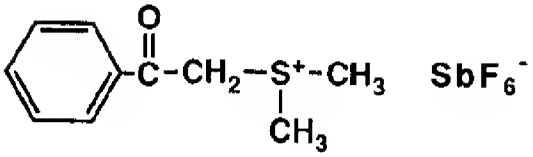
(PAG4-17)

[0094]

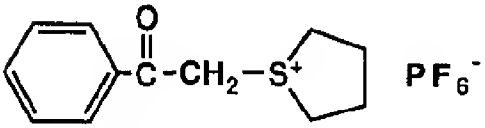
[Formula 47]



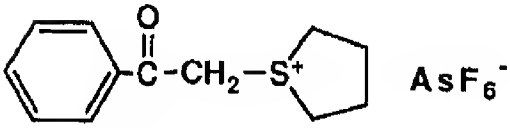
(PAG4-18)



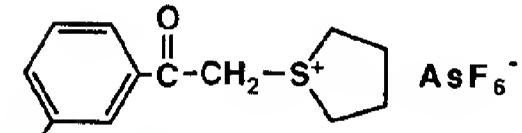
(PAG4-19)



(PAG4-20)



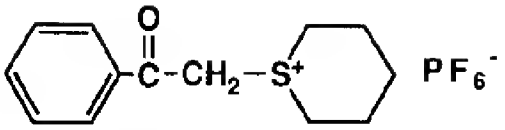
(PAG4-21)



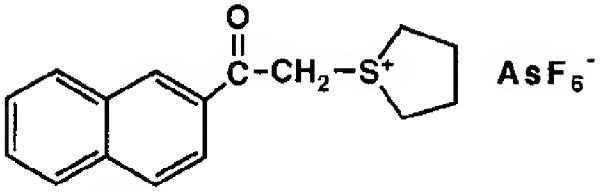
(PAG4-22)

[0095]

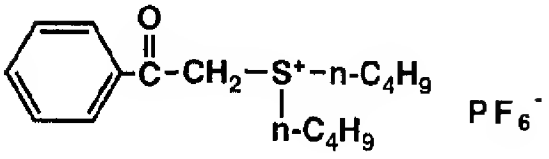
[Formula 48]



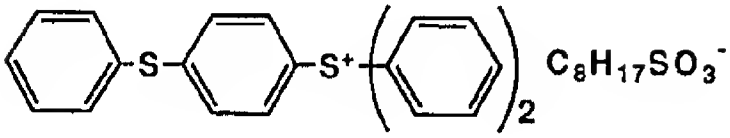
(PAG4-23)



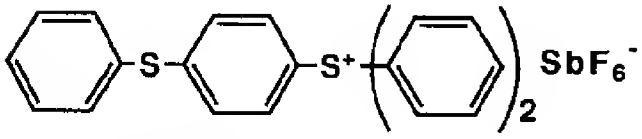
(PAG4-24)



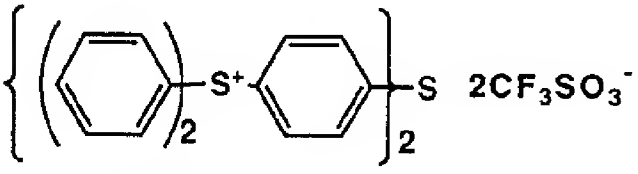
(PAG4-25)



(PAG4-26)



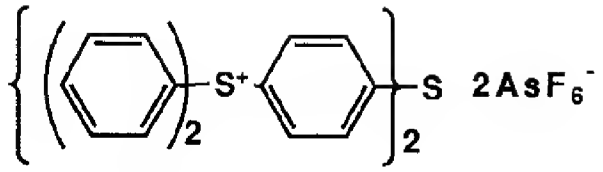
(PAG4-27)



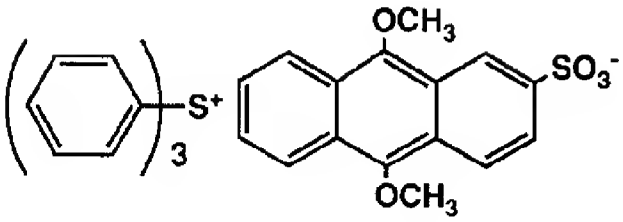
(PAG4-28)

[0096]

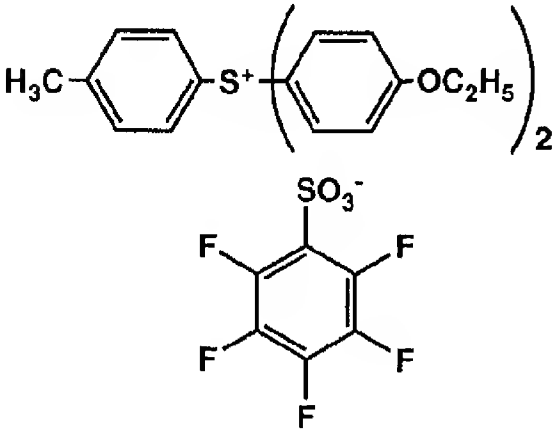
[Formula 49]



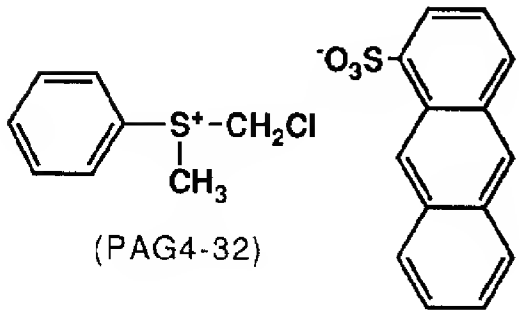
(PAG4-29)



(PAG4-30)



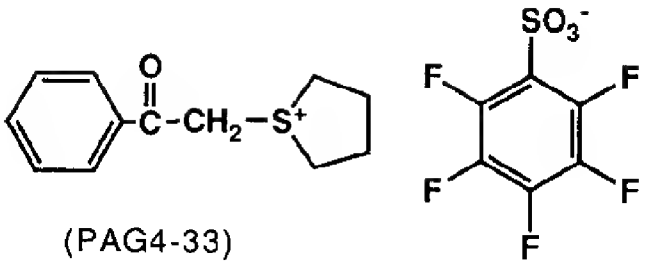
(PAG4-31)



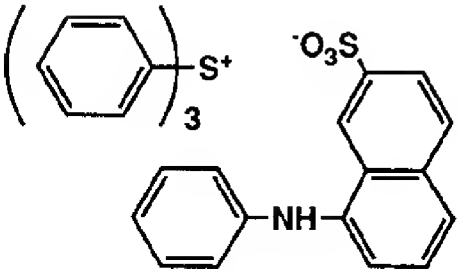
(PAG4-32)

[0097]

[Formula 50]



(PAG4-33)



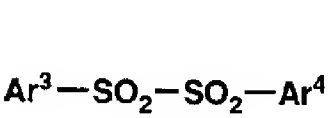
(PAG4-34)

[0098]General formula (PAG3) The above-mentioned onium salt shown by (PAG4) is publicly known, ** It obtains. ** J.W.Knapczyk etal, J.Am.Chem.Soc., 91,145 (1969), A.L. (Maycok etal, J.Org.Chem., 35 and 2532, 1970), E. Goethas etal, Bull.Soc.Chem.Belg., and 73 and 546 (1964), H.M. Leicester, J.Ame.Chem.Soc., 51, 3587 (1929), J. V.Crivello etal, J.Polym.Chem.Ed., 18 and 2677 (1980), U.S. Pat. No. 2,807,648 and said 4,247,473 No., provisional publication of a patent It is compoundable by the method of a statement to No. 101,331 [Showa 53 to] etc.

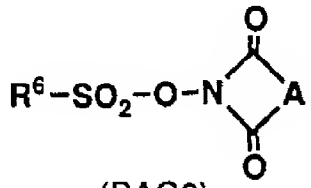
[0099](3) An imino sulfonate derivative expressed with a disulfon derivative or a general formula (PAG6) expressed with a following general formula (PAG5).

[0100]

[Formula 51]



(PAG5)

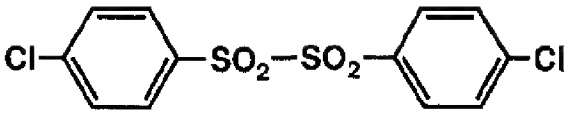


(PAG6)

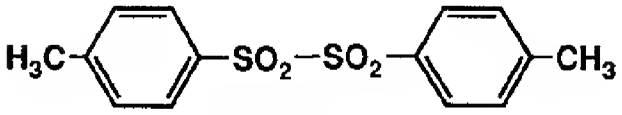
[0101]Ar^3 in a formula and Ar^4 show respectively the aryl group which is not replaced [substitution or] independently. R^6 shows the alkyl group which is not replaced [substitution or] and an aryl group. A shows the alkylene group which is not replaced [substitution or], an alkenylene group, and an allylene group. Although the compound shown below as an example is mentioned, it is not limited to these.

[0102]

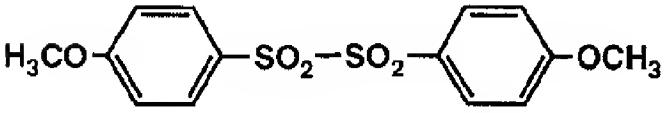
[Formula 52]



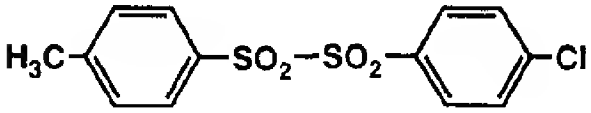
(PAG5-1)



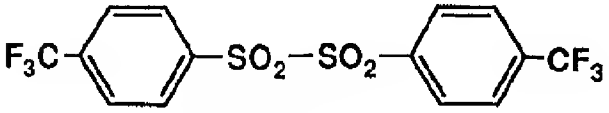
(PAG5-2)



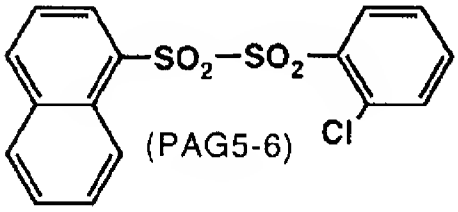
(PAG5-3)



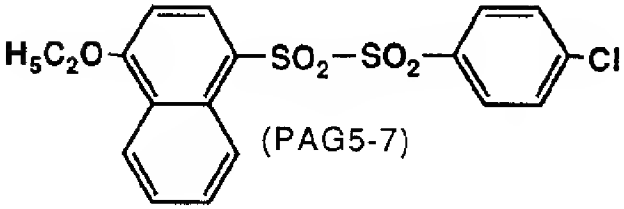
(PAG5-4)



(PAG5-5)



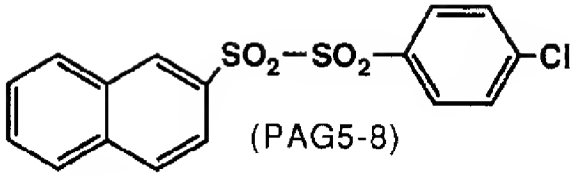
(PAG5-6)



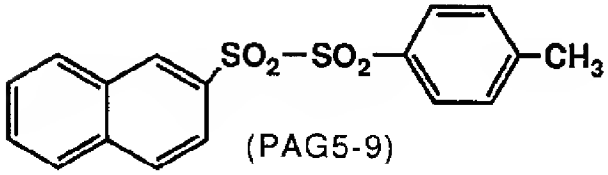
(PAG5-7)

[0103]

[Formula 53]



(PAG5-8)



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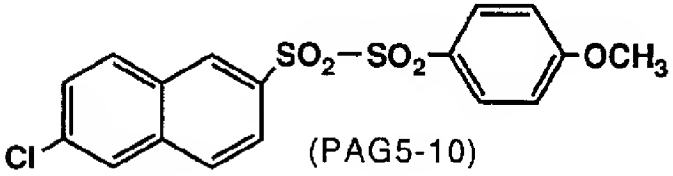
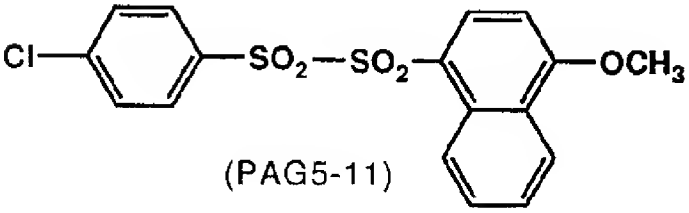
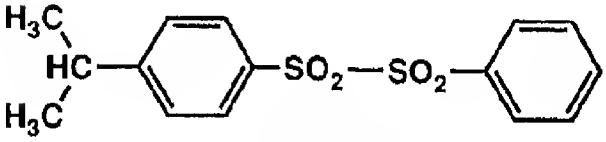


(PAG5-10)



(PAG5-11)



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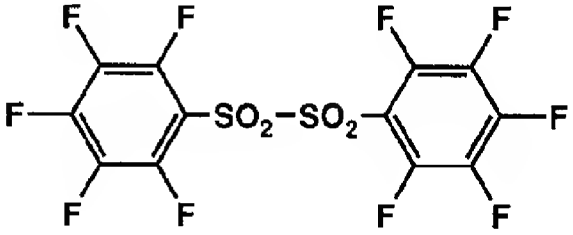
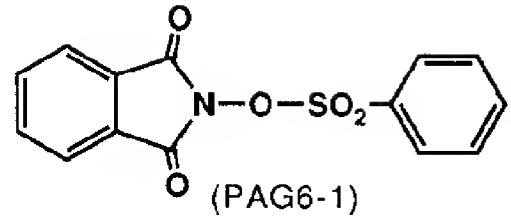


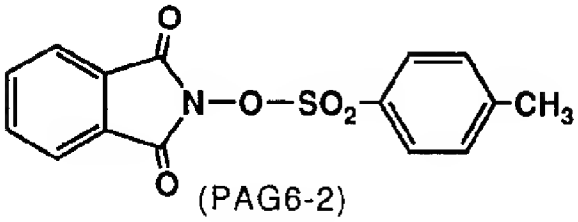
(PAG5-13)

[0104]

[Formula 54]



(PAG6-1)



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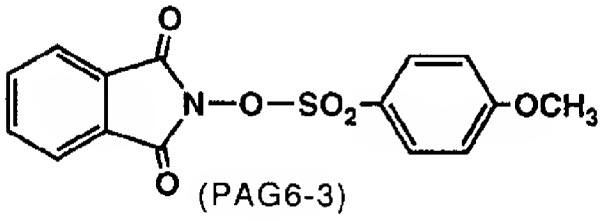
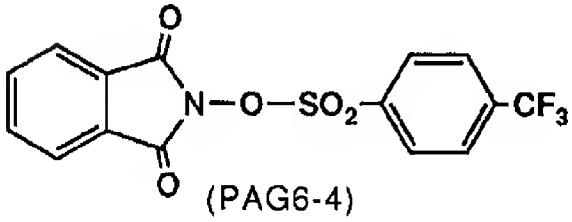
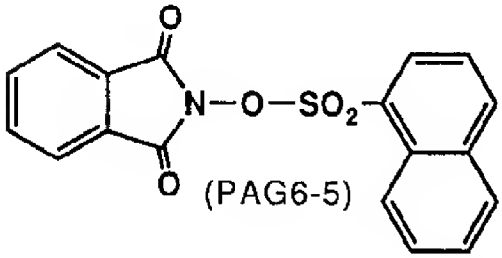


(PAG6-3)



(PAG6-4)



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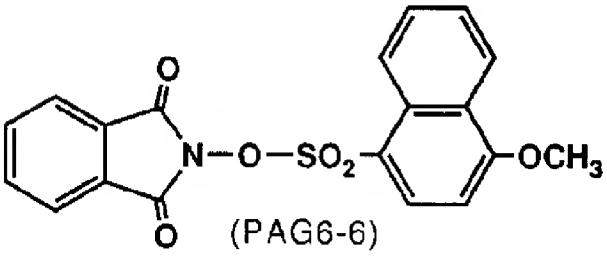
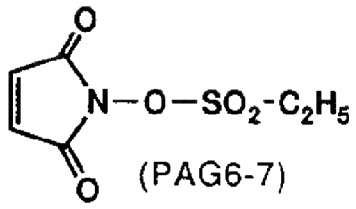


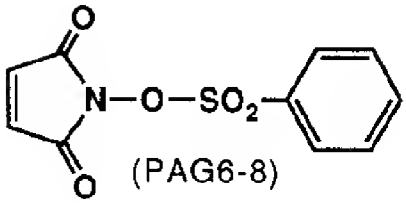
(PAG6-6)

[0105]

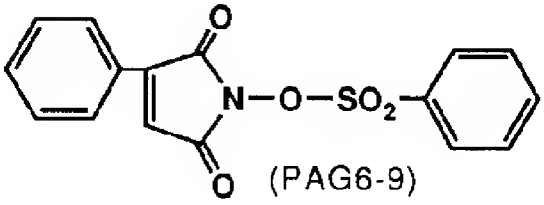
[Formula 55]



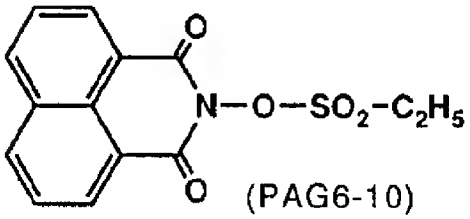
(PAG6-7)



(PAG6-8)



(PAG6-9)



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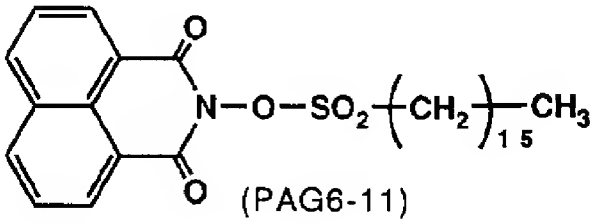

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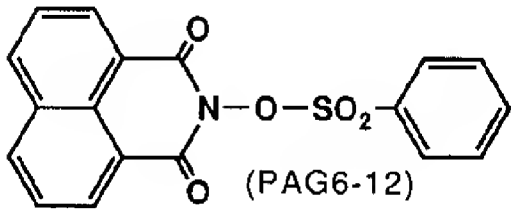
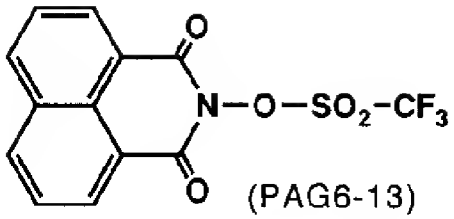


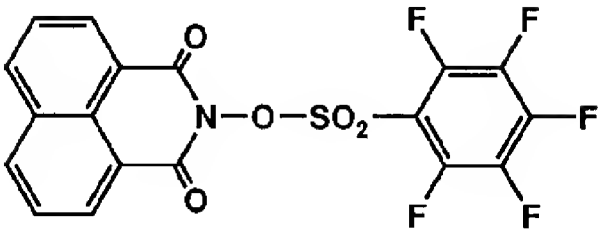
(PAG6-12)

[0106]

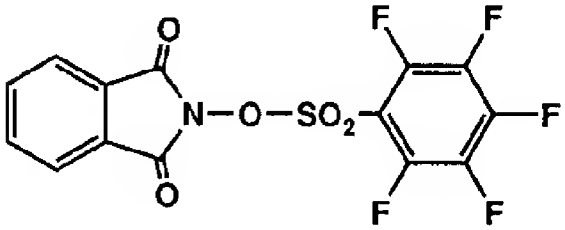
[Formula 56]



(PAG6-13)



(PAG6-14)



(PAG6-15)

[0107]An addition of a compound which decomposes by the exposure of such active light or radiation, and generates acid, It is usually used in 0.001 to 40% of the weight of the range on the basis of full weight (except for a coating solvent) of a photosensitive composition, and is preferably used in 0.1 to 5% of the weight of the range still more preferably 0.01 to 20% of the weight.

[0108]A photosensitive composition of this invention can be made to contain a compound etc. which have two or more phenolic OH radicals which promote solubility over a color, paints, a plasticizer, a surface-active agent, a photosensitizer, and a developing solution if needed. There are fat dye and a basic stain as a suitable color. Specifically Oil yellow #101, oil yellow #103, oil pink #312, oil green BG, Oil blue BOS and oil blue #603, the oil black BY, Oil black BS, the oil black T-505 (above Orient chemical industry incorporated company make), Crystal Violet (CI42555), Methyl Violet (CI42535), rhodamine B (CI45170B), malachite green (CI42000), methylene blue (CI52015), etc. can be mentioned.

[0109]Sensitivity can be given to i or g line for a photosensitive composition of this invention by making a long wavelength field carry out sensitization from far-ultraviolet [in which adds a spectral sensitization agent which is listed below and a photo-oxide generating agent to be used does not have absorption]. As a suitable spectral sensitization agent, specifically Benzophenone, p,p'-tetramethyldiaminobenzophenone, P,p'-tetraethyl ethylamino benzophenone, 2-chloro thioxan ton, Antron, 9-ethoxyanthracene, anthracene, pyrene, perylene, Phenothiazin, benzyl, an acridine orange, a benzoflavin, Setoflavine T,

9,10-diphenylanthracene, 9-fluorenone, An acetophenone, phenanthrene, 2-nitrofluorene, 5-nitroacenaphthene, Benzoquinone, a 2-chloro-4-nitroaniline, N-acetyl-p-nitroaniline, P-nitroaniline, N-acetyl-4-nitro 1-naphthylamine, PIKURAMIDO, anthraquinone, 2-ethylanthraquinone, 2-tert-butylanthraquinone 1,2-benz Anthraquinone, Although it is 3-methyl-1,3-diaza-1,9-benz anthrone, dibenzal acetone, 1,2-naphthoquinone, a 3,3'-carbonyl screw (5,7-dicarbomethoxycoumarin), coronene, etc., it is not limited to these.

[0110]A surface-active agent can also be added to a solvent of this invention (d). Specifically Polyoxyethylene lauryl ether, polyoxyethylene stearylether, Polyoxyethylene alkyl ether, such as polyoxyethylene cetyl ether and polyoxyethylene oleylether. Polyoxyethylene alkyl aryl ether, such as polyoxyethylene octylphenol ether and polyoxyethylene nonyl phenol ether. Polyoxyethylene polyoxypropylene block copolymer. Sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, Sorbitan fatty acid ester species, such as sorbitan monooleate, sorbitan trioleate, and sorbitan tristearate, Polyoxyethylene sorbitan monolaurate, polyoxyethylene sorbitan monopalmitate, Polyoxyethylenesorbitan monostearate, polyoxyethylene sorbitan trioleate, The Nonion system surface-active agents, such as polyoxyethylene sorbitan fatty acid ester, such as polyoxyethylene sorbitan tristearate, EFUTOPPUEF301, EF303, EF352 (made in new Akita Chemicals), The megger fuck F171, F173 (made by Dainippon Ink), Fluorad FC430, FC431 (made by Sumitomo 3M), Fluorochemical surfactants, such as Asahi guard AG710, the Sir chlorofluocarbon S-382, SC101, SC102, SC103, SC104, SC105, and SC106 (made by Asahi Glass Co., Ltd.), Organosiloxane polymer KP341 (made by Shin-Etsu Chemical Co., Ltd.), an acrylic acid series or methacrylic acid series (**) polymerization poly flow No.75, No.95 (product made from Kyoeisha Fatty chemistry Industry), etc. can be mentioned. Loadings of these surface-active agents of below the amount part of duplexs are usually one or less weight section preferably per solid content 100 weight section in a constituent of this invention. It may add independently and these surface-active agents can also be added in some combination.

[0111]The above-mentioned photosensitive composition on a substrate (example: silicon / diacid-ized silicon covering) which is used for manufacture of a precision integrated circuit device A spinner, A good resist pattern can be obtained by exposing through a predetermined mask after spreading with suitable coating methods, such as a coating machine, and developing negatives by performing bake.

[0112]As a developing solution of a photosensitive composition of this invention, sodium hydroxide, a potassium hydrate, Inorganic alkali, such as sodium carbonate, a sodium silicate, metasilicic acid sodium, and an ammonia solution. Primary amines, such as ethylamine and n-propylamine, diethylamine, Tertiary amines, such as secondary amines, such as di-n-butylamine, triethylamine, and methyldiethylamine. Alcohol amines, such as dimethylethanolamine and triethanolamine. Alkaline aqueous solutions, such as cyclic amines, such as quarternary ammonium salt, such as tetramethylammonium hydroxide and tetraethylammoniumhydroxide, pyrrole, and PIHERIJIN, can be used. concentration of such alkali -- normal concentration -- 0.001-1N -- desirable -- 0.01-0.50N -- it is used in 0.03-0.30N still more preferably. Alcohols and a surface-active agent can also be used for the above-mentioned alkaline aqueous solution, carrying out adequate amount addition. Hereafter, although an example explains this invention still in detail, thereby, the contents of this invention are not limited.

[0113]

[Example]

[Synthetic example-1 of a lysis inhibition agent compound] alpha, alpha', and the alpha''-tris (4-hydroxyphenyl)-1,3,5-triisopropyl benzene 20g were dissolved in 400 ml of tetrahydrofurans. The tert-FU ** TOKISHI potassium 14g was added to this solution under a nitrogen atmosphere, and 29.2 g of di-tert-butyl dicarbonate was added after stirring for 10 minutes at the room temperature. Under the room temperature, it was made to react for 3 hours, ice water was filled with reaction mixture, and ethyl acetate extracted output. Backwashing by water of the ethyl acetate layer was carried out further, and the dried back solvent was distilled off. After recrystallizing the obtained crystalline solid (diethylether), it was made to dry and 25.6 g of examples of a compound (all 31:R is t-BOC groups) were acquired.

[0114][Synthetic example-2 of a lysis inhibition agent compound] alpha, alpha', and the alpha''-tris (4-hydroxyphenyl)-1,3,5-triisopropyl benzene 20g were dissolved in 400 ml of diethylether. The chloride of 31.6 g of 3,4-dihydro-2H-Piran and a catalyst amount was added to this solution, and was made to react to it under reflux under a nitrogen atmosphere for 24 hours. After ending reaction, a small amount of sodium hydroxide was added, and it filtered. The output acquired by distilling off the solvent of filtrate was refined by the column chromatography, it was made to dry and the example of a compound (all 31:R is THP groups) was acquired.

[0115][Synthetic example-3 of a lysis inhibition agent compound] In alpha, alpha', and 120 ml of N,N-dimethylacetamide solution of the alpha''-tris (4-hydroxyphenyl)-1,3,5-triisopropyl benzene 19.2g (0.040 mol). The potassium carbonate 21.2g (0.15 mol) and also 27.1 g (0.14 mol) of bromoacetic acid t-butyl were added, and it agitated at 120 ** for 7 hours. The reaction mixture was fed into the water 1.5l after that, and ethyl acetate extracted. The extract was condensed after desiccation with magnesium sulfate, and as a result of refining in a column chromatography (carrier: silica gel and developing solvent:ethyl acetate / n-hexane =3 / 7 (volume ratio)), the light yellow consistency solid 30g was obtained. By NMR, it checked that this was an example of a compound (all 31:R is $-CH_2COOC_4H_9^t$ groups).

[0116][Synthetic example-4 of a lysis inhibition agent compound] The 1-[alpha-methyl-alpha-(4'-hydroxyphenyl) ethyl]-4-[alpha' and alpha'-bis(4''-hydroxyphenyl)ethyl] benzene 42.4g (0.10 mol) is dissolved in 300 ml of N,N-dimethylacetamide, The potassium carbonate 49.5g (0.35 mol) and 84.8 g (0.33 mol) of bromoacetic acid cumyl ester were added to this. Then, it agitated at 120 ** for 7 hours. After it fed the reaction mixture into the ion exchange water 2l and acetic acid neutralized, ethyl acetate extracted. The ethyl acetate extract was condensed, it refined like the synthetic example [3], and 70 g of examples of a compound (all 18:R is $-CH_2COOC(CH_3)_2C_6H_5$ groups) were acquired.

[0117][Synthetic example-5 of a lysis inhibition agent compound] In 120 ml of alpha, alpha, alpha', alpha', and alpha''alpha'' N,N-dimethylacetamide solution of the - hexakis (4-hydroxyphenyl)-1,3,5-triethylbenzene 14.3g (0.020 mol). The potassium carbonate 21.2g (0.15 mol) and also 27.1 g (0.14 mol) of bromoacetic acid t-butyl were added, and it agitated at 120 ** for 7 hours. Then, the reaction mixture was fed into the water 1.5l, and ethyl acetate extracted. The extract was condensed after desiccation with magnesium sulfate, and as a result of refining in a column chromatography (carrier: silica gel and developing solvent:ethyl acetate / n-hexane =2 / 8 (volume ratio)), the light yellow granular material 24g was obtained. By NMR, it checked that this was an example of a compound (all 62:R is $-CH_2-COO-C_4H_9^t$ groups).

[0118][Synthetic example-6 of a lysis inhibition agent compound] alpha, alpha', and the alpha''-tris (4-hydroxyphenyl)-1,3,5-triisopropyl benzene 20g (0.042 mol) were dissolved in 400 ml of tetrahydrofurans

(THF). t-butoxypotassium 9.3g (0.083 mol) was added to this solution under a nitrogen atmosphere, and 19.5 g (0.087 mol) of di-t-butyldicarbonate was added after churning for 10 minutes at the room temperature. Under the room temperature, it was made to react for 3 hours, ice water was filled with reaction mixture, and ethyl acetate extracted output. As a result of condensing an ethyl acetate extract and carrying out judgment refining in a column chromatography (carrier: silica gel and developing solvent:ethyl acetate / n-hexane =1 / 5 (volume ratio)), 7 g of examples of a compound (as for 31:2 R, a t-BOC group and one R are hydrogen atoms) were acquired.

[0119][Synthetic example-7 of a lysis inhibition agent compound] alpha, alpha', and the alpha"-tris (4-hydroxyphenyl)-1,3,5-triisopropyl benzene 48.1g (0.10 mol) are dissolved in 300 ml of dimethylacetamide, The potassium carbonate 22.1g (0.16 mol) and 42.9 g (0.22 mol) of bromoacetic acid t-butyl were added to this. Then, it agitated at 120 ** for 5 hours. After it fed the reaction mixture into the ion exchange water 2l and acetic acid neutralized, ethyl acetate extracted. condensing an ethyl acetate extract -- a column chromatography (carrier: -- silica gel.) Developing solvent: As a result of carrying out judgment refining in ethyl acetate/n-hexane =1 / 5 (volume ratio), 10 g of examples of a compound (as for 31:2 R, a $-CH_2-COO-C_4H_9^t$ group and one R are hydrogen atoms) were acquired.

[0120][The synthetic example of novolak resin] Teaching the m-cresol 40g, 60 g of p-cresol, 49g of 37% formalin aqueous solution, and the oxalic acid 0.13g to 3 mouth flask, and stirring them, temperature up was carried out and it was made to react to 100 ** for 15 hours. Temperature was raised to 200 ** after that, it decompressed to 5mmHg gradually, and water, an unreacted monomer, formaldehyde, oxalic acid, etc. were removed. Subsequently, the fused alkali meltable novolak resin (NOV.3) was returned to the room temperature, and was collected. The obtained novolak resin (NOV.3) was the weight average molecular weight 7100 (polystyrene conversion).

[0121]Similarly, novolak resin of the following which changed monomer composition was compounded. NOV.1 m-cresol / p-cresol = 60/40, Mw=12,000 NOV.2 m-cresol / p-cresol = 50/50 and Mw=8,700 NOV.4 m-cresol / p-cresol / 3,5-xylenol =25/50/28, and Mw=5,200. NOV.5 m-cresol / 2,3,5-trimethyl phenol = 55/57, Mw=5,800[0122]After dissolving thoroughly 20 g of novolak resin (NOV.3) obtained above in the methanol 60g, in addition, the pitch was settled gradually, stirring the water 30g to this. Collected the pitches which removed the upper layer by the decantation and precipitated, heated at 40 **, it was made to dry under decompression for 24 hours, and alkali solubility novolak resin (NOV.6) was obtained. Weight average molecular weight was 8000 (polystyrene conversion).

[0123]The m-cresol 85g, 15 g of p-cresol, and 53 g of 37% formalin aqueous solution were taught to 3 mouth flask, and it stirred well, heating with a 110 ** oil bath, 2.4g of zinc acetate dihydrate was added, and heating stirring was performed for 5 hours. Subsequently, after having continued the same cresol mixture 100g and 47 g of formalin aqueous solution, teaching the same flask and continuing heating stirring further for 1 hour, temperature was lowered to 80 ** and the oxalic acid 0.2g was added. The temperature of the oil bath was kept at 110 **, and it was made to react by a reflux condition again for 15 hours. Contents were opened in the water containing 1% of chloride after that, and the resultant was extracted of ethyl Cellosolve acetate. Subsequently, this was moved to the vacuum distillation machine, and temperature was raised to 200 **, and it dried, and also distillation was performed under decompression of 2 - 3mmHg for 2 hours, and the residual monomer was removed. Melting polymer was collected from the flask and target novolak resin

(NOV.7, Mw=7,500) was obtained.

[0124]Resist was prepared using the compound of this invention shown in Example 1 - the example of the 19 above-mentioned composition. The formula at that time is shown in Table 1.

[0125]Resist was prepared with solvents other than this invention (d) using the compound of this invention shown in the comparative example 1 - the example of the 3 above-mentioned composition. The formula at that time is shown in Table 1.

[0126]In accordance with the method written in the comparative example 4,5 U.S. Pat. No. 4,491,628 specification, t-buthoxycarbonyloxy styrene polymer and t-buthoxycarbonyloxy alpha-methylstyrene polymer were compounded, and the two-component system positive resist was prepared. The formula at that time is shown in Table 1.

[0127]3 component-system positive resist was prepared by making into a lysis inhibition agent the compound di-t-butyl terephthalate written in the six to comparative example 8 European patent No. 249,139 specification, 4-t-butoxy-p-biphenyl, and t-butyl-2-naphthyl carbonate. The formula at that time is shown in Table 1.

[0128]

[Table 1]

表1：感光性組成物の処方

	アルカリ可溶性樹脂(g)	光酸発生剤 (g)	溶解阻止剤 (g)	酸分解性基	溶剤 (重量比)
実施例 1	NOV.7 1.5	PAG3-3 0.05	化合物(1) 0.55	TBOC	MMP
実施例 2	NOV.6 1.5	PAG4-3 0.05	化合物(6) 0.55	TBE	PGMA
実施例 3	NOV.4 1.5	PAG4-5 0.05	化合物(10) 0.55	THP	EL/EEP = 6/4
実施例 4	NOV.3 1.5	PAG4-7 0.05	化合物(10) 0.55	TBE	HP
実施例 5	NOV.5 1.5	PAG4-5 0.05	化合物(12) 0.55	CUE	PGMA
実施例 6	NOV.2 1.5	PAG4-4 0.05	化合物(18) 0.55	TBE	MMP/DEGDM = 8/2
実施例 7	NOV.6 1.5	PAG5-4 0.05	化合物(18) 0.55	THP	PGMA
実施例 8	NOV.2 1.5	PAG5-12 0.05	化合物(19) 0.55	TBOC	MMP
実施例 9	NOV.4 1.5	PAG6-15 0.05	化合物(25) 0.55	TBOC	HP
実施例 10	NOV.1 1.5	PAG4-4 0.05	化合物(29) 0.55	CUE	PGMA/DEGDM = 7/3
実施例 11	NOV.3 1.5	PAG4-3 0.05	化合物(31) 0.55	TBOC	MMP
実施例 12	NOV.3 1.5	PAG4-3 0.05	化合物(31) 0.55	TBE	PGMA
実施例 13	NOV.1 1.5	PAG4-5 0.05	化合物(40) 0.55	TBOC	EL/DEGDM = 8/2
実施例 14	PVP 1.5	PAG4-7 0.05	化合物(44) 0.55	TBE	MMP
実施例 15	NOV.3 1.5	PAG6-2 0.05	化合物(60) 0.55	TBE	HP/DEGDM = 7/3
実施例 16	PVP 1.5	PAG4-6 0.05	化合物(60) 0.55	TBOC	PGMA/DEGDM = 7/3
実施例 17	PVP 1.5	PAG4-5 0.05	化合物(62) 0.55	TBE	PGMA
実施例 18	NOV.3 1.5	PAG4-5 0.05	化合物 (31:合成例6) 0.55	TBOC	PGMA
実施例 19	NOV.2 1.5	PAG4-5 0.05	化合物 (31:合成例7) 0.55	TBE	MMP
比較例 1	NOV.3 1.5	PAG4-3 0.05	化合物(31) 0.55	TBE	THF
比較例 2	NOV.3 1.5	PAG4-3 0.05	化合物(31) 0.55	TBOC	IBB
比較例 3	NOV.3 1.5	PAG4-3 0.05	化合物(31) 0.55	TBE	NMP
比較例 4	TBOCS 1.0	PAG4-3 0.1	—	—	PGMA
比較例 5	TBAMS 1.0	PAG4-3 0.1	—	—	PGMA
比較例 6	NOV.3 1.5	PAG4-3 0.05	DTBTP 0.55	—	PGMA
比較例 7	NOV.3 1.5	PAG4-3 0.05	TBPBP 0.55	—	PGMA
比較例 8	NOV.3 1.5	PAG4-3 0.05	TBNC 0.55	—	PGMA

[0129]The cable address used in Table 1 expresses the following contents.

[0130]<Polymer> NOV.1-7 novolak-resin PVP p-hydroxystyrene polymer (weight average molecular weight 9,600) TBOCS t-buthoxycarbonyloxy styrene polymer (number average molecular weight 21,600)

TBAMS t-buthoxycarbonyloxy alpha-methylstyrene polymer (number average molecular weight 46,900)

[0131]<Lysis inhibition agent> DTBTP di-t-butyl terephthalate TBPBP 4-t-butoxy-p-biphenyl TBNC t-butyl-2-naphthyl carbonate[0132]<The acidolysis nature group in a lysis inhibition agent> [0133]

[Formula 57]

TBOC : $-O-COO-C_4H_9^t$

TBE : $-O-CH_2-COO-C_4H_9^t$

CUE : $-O-CH_2-COO-C(CH_3)_2C_6H_5$

THP : 

[0134]< solvent. (The boiling point, **) >** this invention. The solvent EL ethyl lactate (154) MMP of (d). 3-methoxy methyl propionate. (145) Solvent THF tetrahydrofuran (66) DEGDM diethylene glycol dimethyl ether (162) EEP other than PGMA propylene-glycol-monomethyl-ether acetate (146) HP 2-heptanone (151) ** this invention (d). 3-ethoxyethyl propionate (170) IBB 4-isobutoxy-2-butanone (181) NMP N-methyl-2-pyrrolidone (202) [0135][Preparation of a photosensitive composition and evaluation] Each raw material shown in Table 1 was dissolved in the solvent 6g of Table 1, it filtered with a 0.2-micrometer filter, and the resist solution was created. Using the spin coater, this resist solution was applied on the silicon wafer, was dried with the vacuum absorption type hot plate for 110 ** 60 seconds, and the resist film of 1.0 micrometer of thickness was obtained. It exposed by using a 248nmKrF excimer laser stepper (NA=0.42) for this resist film. A 95 ** vacuum absorption type hot plate performed heating for 60 seconds after exposure, and immediately, to Examples 14, 16, and 17, other things were immersed for 60 seconds in tetramethylammonium hydroxide (TMAH) solution 2.38%, and were rinsed and dried with water for 30 seconds 1.19%. Thus, the pattern on the obtained silicon wafer was observed with the scanning electron microscope, and the profile of resist was evaluated. The result is shown in Table 2.

[0136]Sensitivity was defined with the reciprocal of the light exposure reproducing a 0.70-micrometer mask pattern, and the relative value of the sensitivity of the comparative example 1 showed it. Film contraction was expressed in units of percentage of the ratio of exposure of an exposure part, and the thickness before and behind bake. Resolution expresses the marginal resolution in the light exposure reproducing a 0.70-micrometer mask pattern. The resist of the result of Table 2 to this invention has little film decrease by development, and it turns out that it has high sensitivity, high resolving power, and a good profile.

[0137]

[Table 2]

表2：評価結果

	相対感度	現像による膜減り（%）	解像力（μm）	レジストパターンのプロファイル
実施例 1	1.2	2	0.34	良好
実施例 2	1.4	2	0.34	良好
実施例 3	1.3	2	0.35	良好
実施例 4	1.4	1	0.30	良好
実施例 5	1.2	1	0.35	良好
実施例 6	1.4	1	0.30	良好
実施例 7	1.1	2	0.34	良好
実施例 8	1.2	1	0.34	良好
実施例 9	1.2	1	0.35	良好
実施例 10	1.5	1	0.35	良好
実施例 11	1.4	1	0.30	良好
実施例 12	1.4	1	0.30	良好
実施例 13	1.4	1	0.32	良好
実施例 14	1.5	1	0.30	良好
実施例 15	1.2	1	0.30	良好
実施例 16	1.4	2	0.28	良好
実施例 17	1.4	1	0.30	良好
実施例 18	1.8	2	0.28	良好
実施例 19	1.8	2	0.28	良好
比較例 1	0.9	3	0.35	良好
比較例 2	1.4	4	0.37	ややテーパー
比較例 3	1.4	4	0.37	ややテーパー
比較例 4	1.0	4	0.40	テーパー
比較例 5	0.9	4	0.40	テーパー
比較例 6	1.1	15	0.45	テーパー
比較例 7	1.3	19	0.45	テーパー
比較例 8	1.3	23	0.47	テーパー

[0138]

[Effect of the Invention]There is little film decrease after development, and it is high sensitivity and high resolving power, and the chemical amplification type positive type photosensitive composition of this invention which contains the solvent whose boiling point is 130–155 ** not less than 30% has a good profile.

[Translation done.]

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7/004	５０１			
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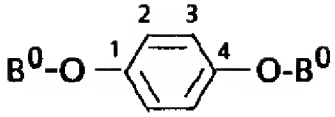
(54)【発明の名称】　ポジ型感光性組成物



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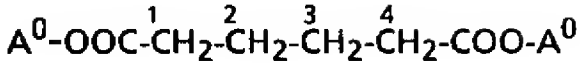

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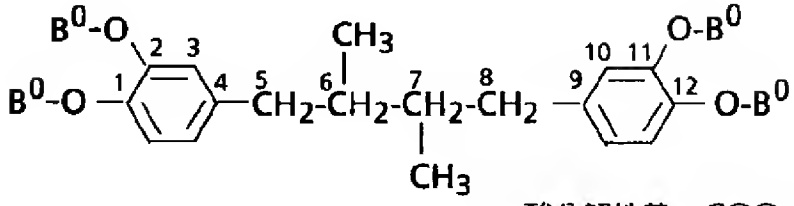
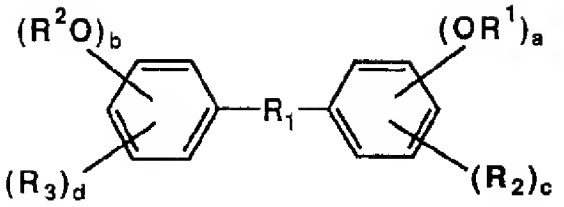


(3)

酸分解性基：-COO-A^0, -O-B^0



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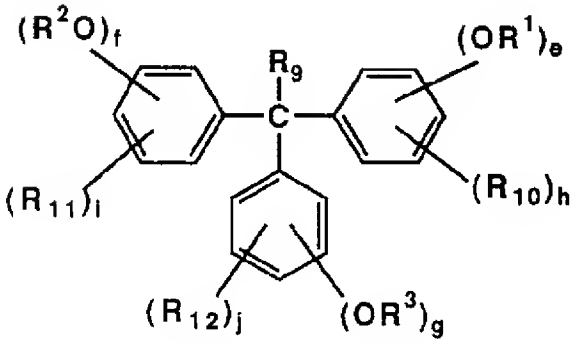

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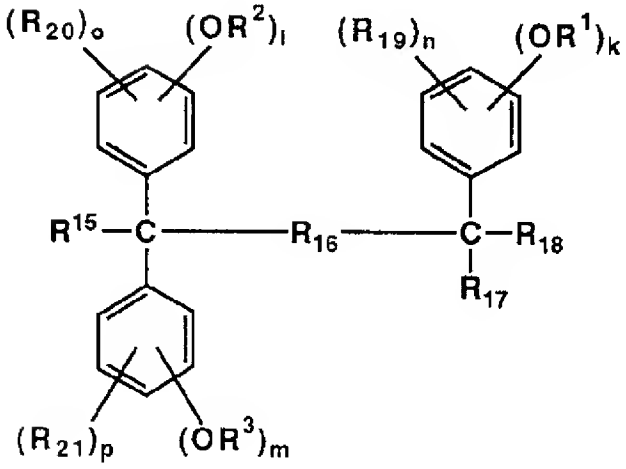

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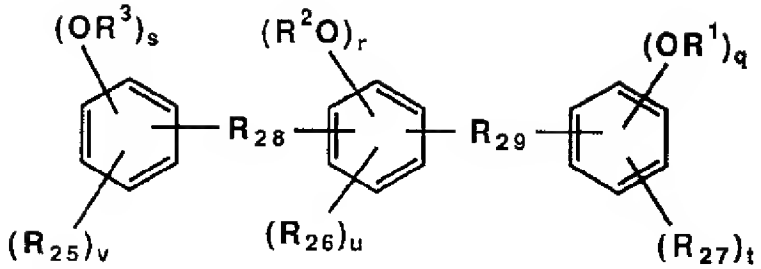

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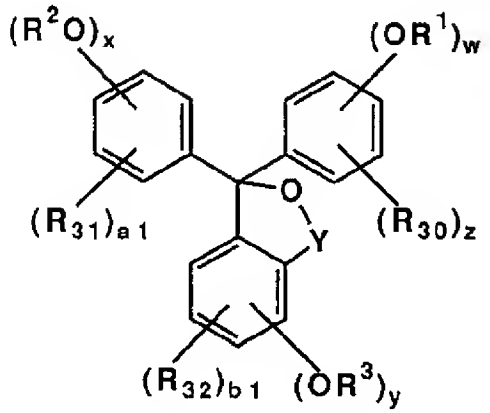

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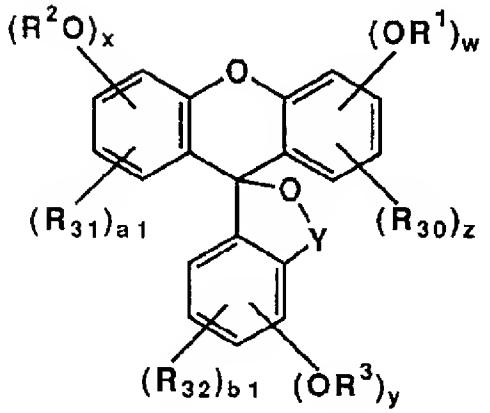

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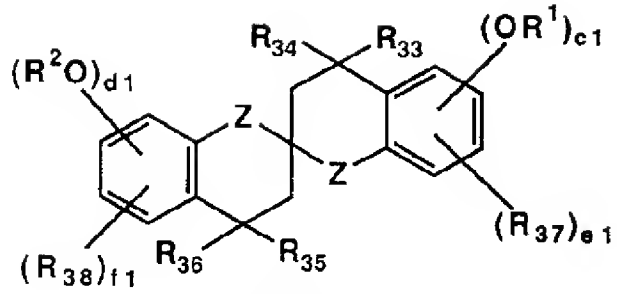
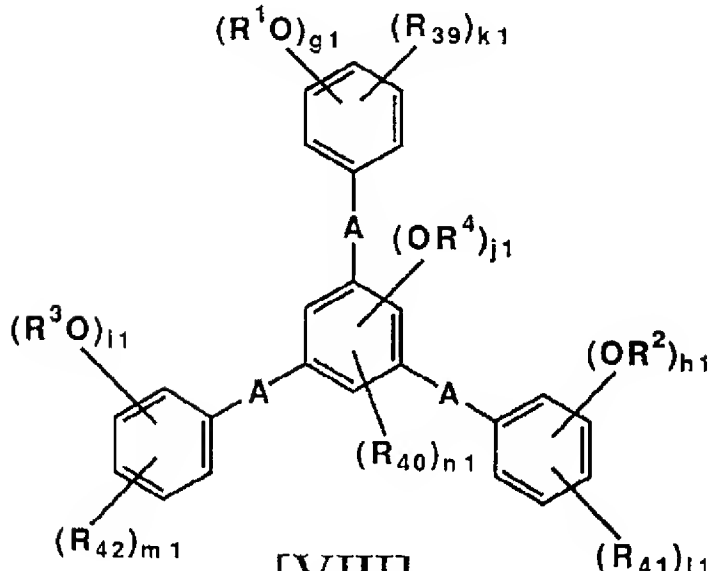
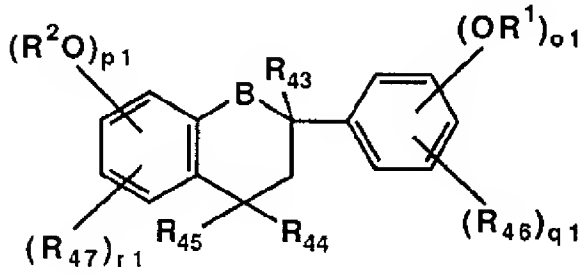

R34
R33
(OR1)c1
(R2O)d1
Z
Z
(R37)e1
(R38)f1
R36
R35

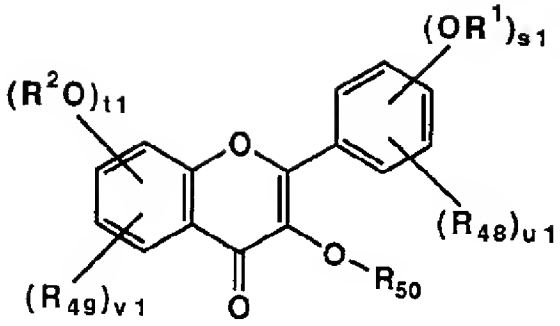
[VII]


(R1O)g1
(R39)k1
A
(OR4)j1
(R3O)i1
A
A
(OR2)h1
(R40)n1
(R42)m1
(R41)l1

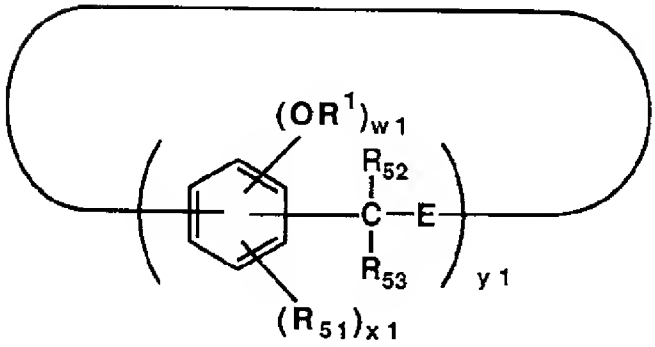
[VIII]


(OR1)o1
(R2O)p1
R43
B
(R46)q1
(R47)r1
R45
R44

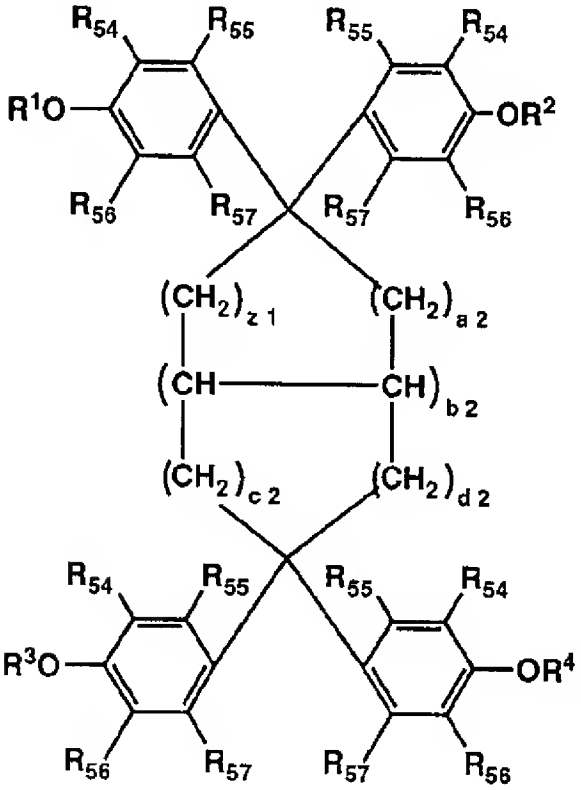
[IX]



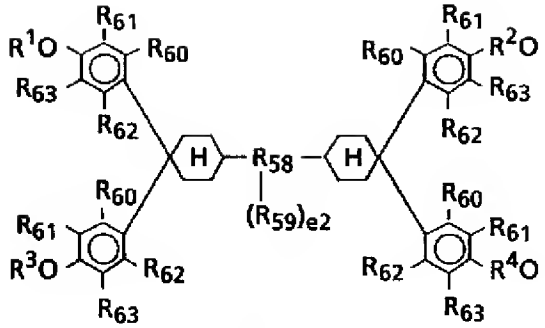
[X]



[XI]



[XII]

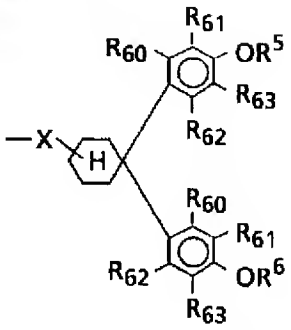


(XIII)

ここで、

R_{58} ：有機基、単結合、-S-、-SO-もしくは 

R_{59} ：水素原子、一価の有機基もしくは

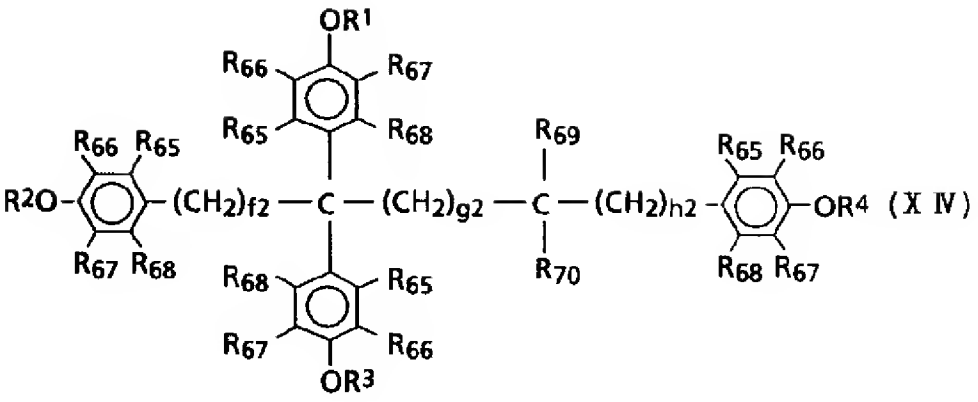


R_{60}～R_{63}：同一でも異なっていても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、アルケニル基、但し、少なくとも2つは
－O-R0-COO-A0基もしくは－O-B0基である、又、各4もしくは6個の同一記号の置換基は同一の基でなくても良い、

X ：2価の有機基、

e2 ：0もしくは1、

を表す。

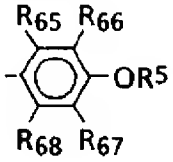


(XIV)

ここで、

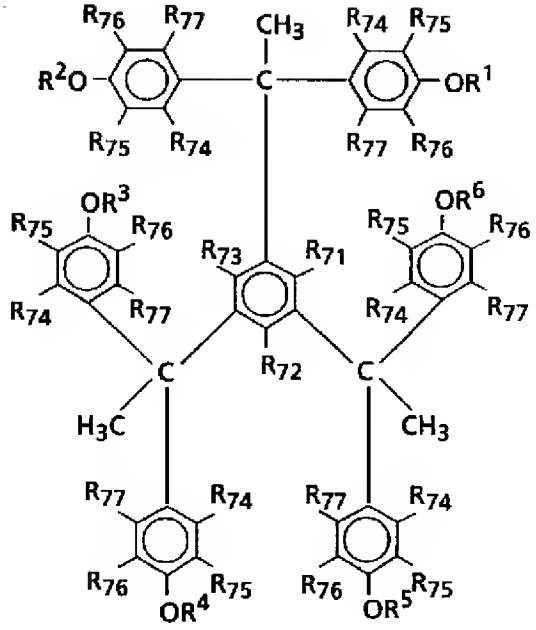
R_{65}~R_{68}：同一でも異なっても良く水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基もしくはアルケニル基、但し、各4~6個の同一記号の置換基は同一の基でなくても良い、

R_{69}, R_{70} ：水素原子、アルキル基もしくは



f2, g2, h2：0もしくは1~5の整数、

を表す。



(XV)

ここで、

R_{71}~R_{77}: 同一でも異なっても良く、水素原子、水酸基、ハロゲン原子、アルキル基、アルコキシ基、ニトロ基、アルケニル基、アリール基、アラルキル基、アルコキシカルボニル基、アリールカルボニル基、アシロキシ基、アシル基、アラルキルオキシ基もしくはアリールオキシ基、但し、各6個の同一記号の置換基は同一の基でなくても良い、

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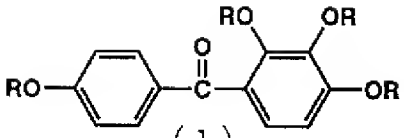

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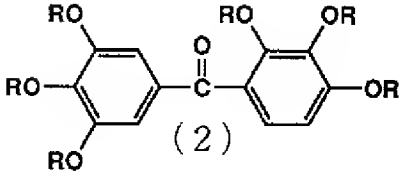

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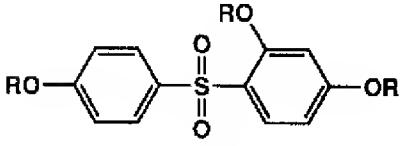

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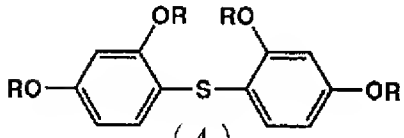

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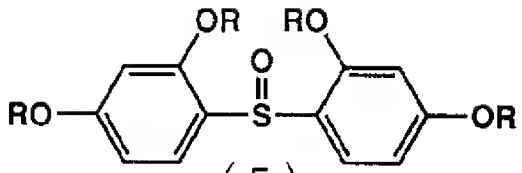

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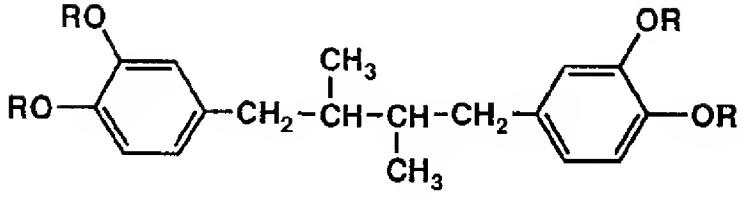

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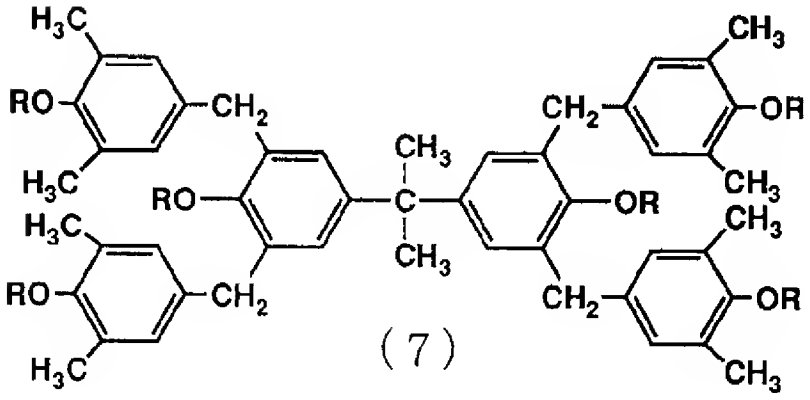

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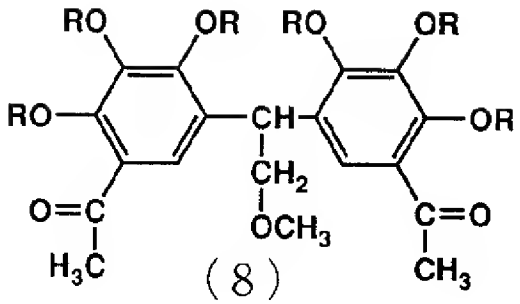
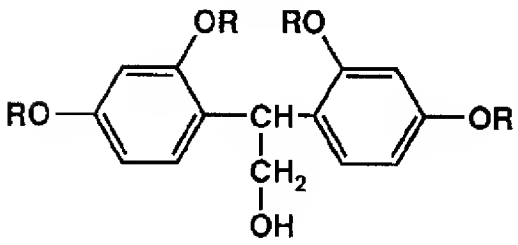
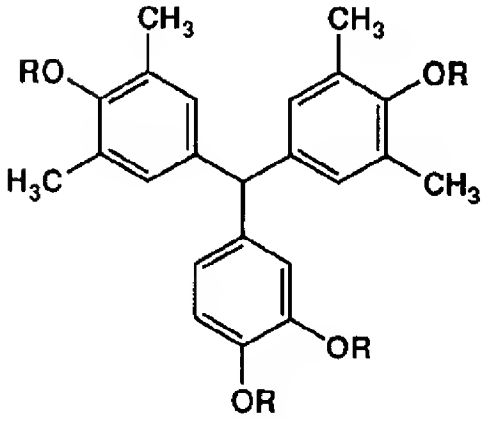

RO
OR
RO
OR
RO
CH
OR
CH2
O=C
OCH3
C=O
H3C
CH3

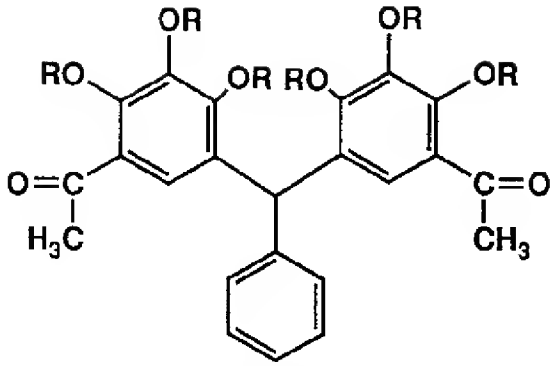
(8)


OR
RO
RO
CH
OR
CH2
OH

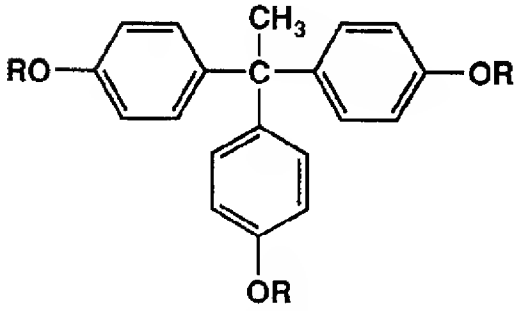
(9)


CH3
CH3
RO
OR
H3C
CH3
OR
OR

(10)



（１４）



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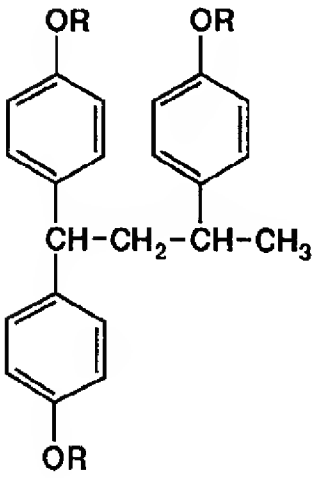
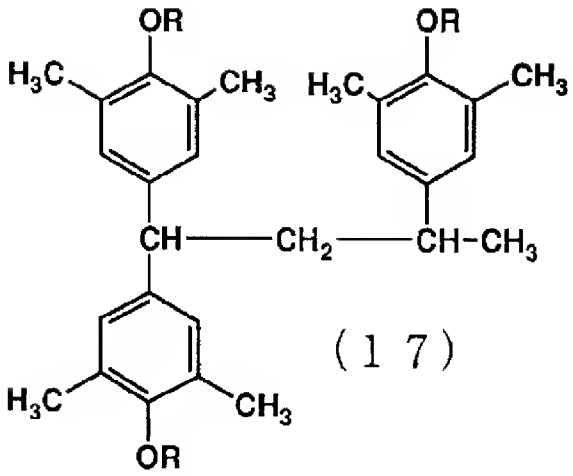


（１６）



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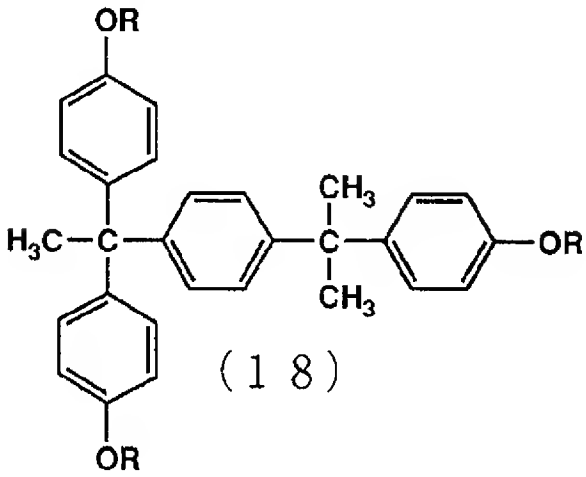
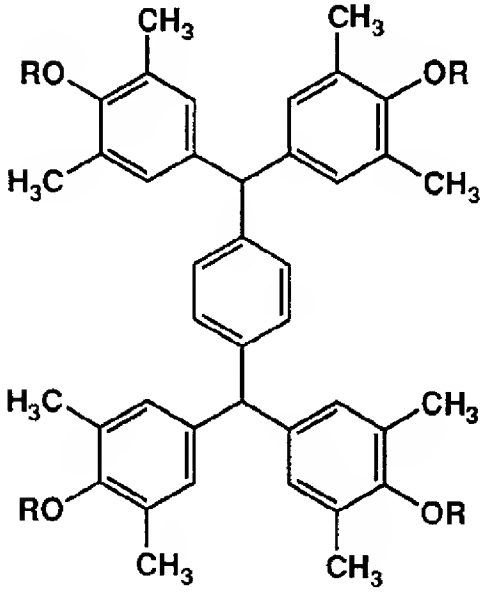


(18)



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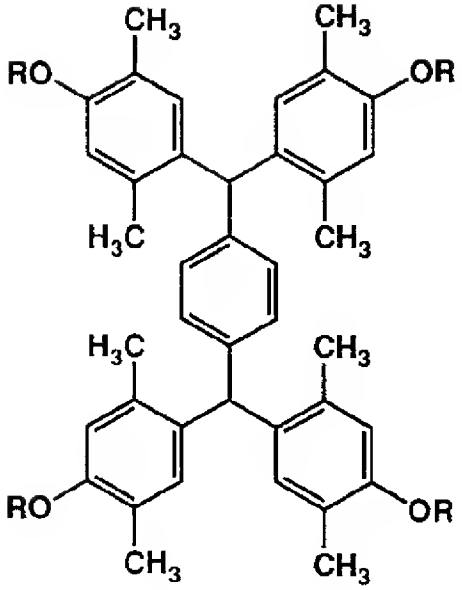
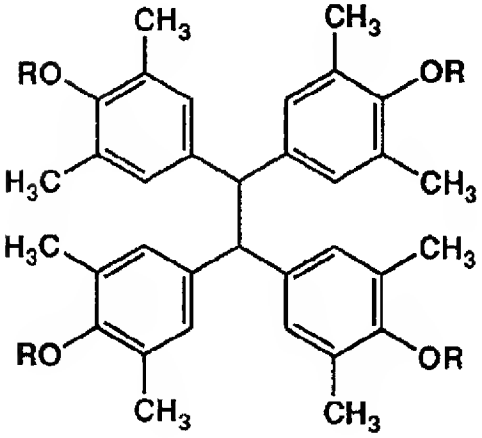
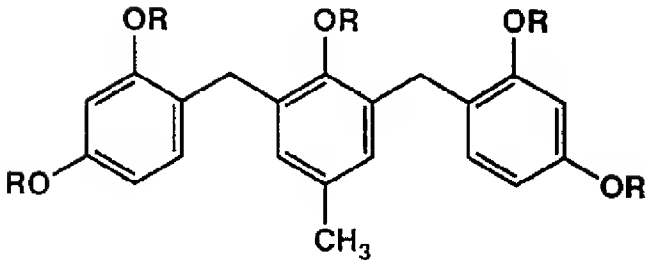


(20)



(21)



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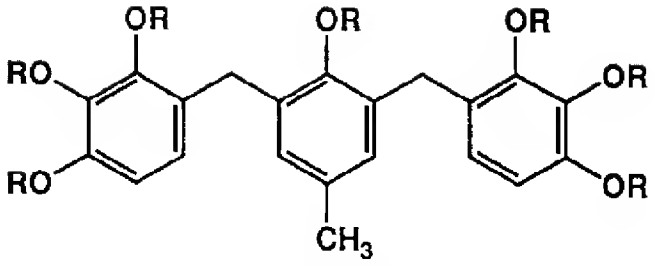
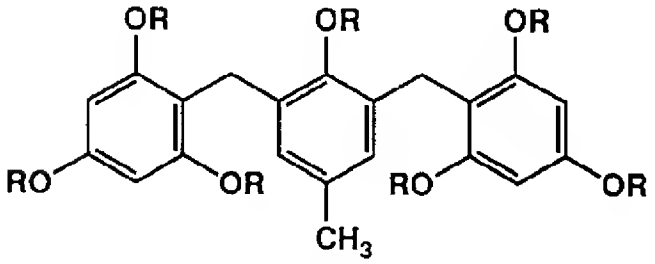
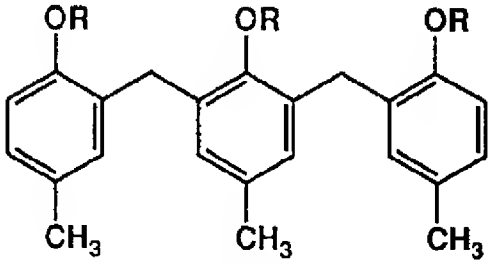

OR
OR
OR
RO
OR
RO
OR
CH3

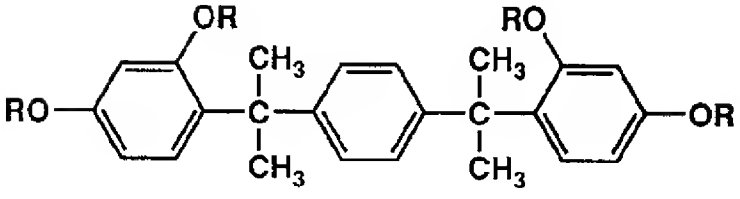
(23)


OR
OR
OR
RO
OR
RO
OR
CH3

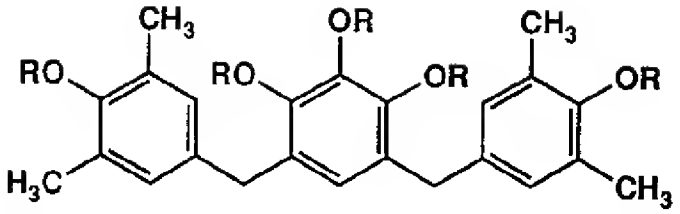
(24)


OR
OR
OR
CH3
CH3
CH3

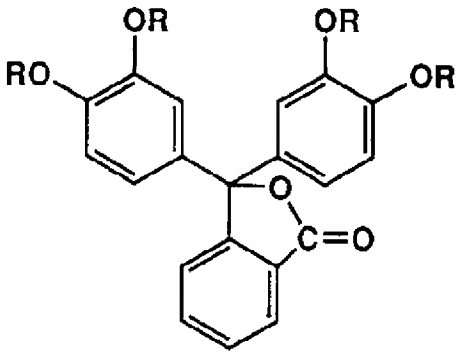
(25)


OR
RO
CH3
CH3
RO
C
C
OR
CH3
CH3

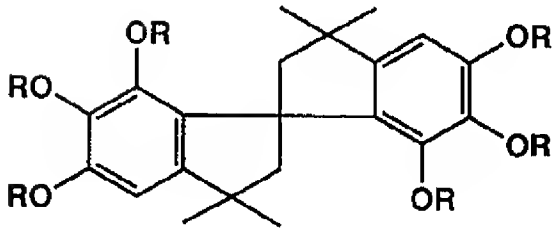
(26)



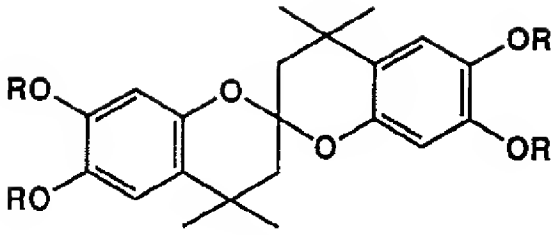
(27)



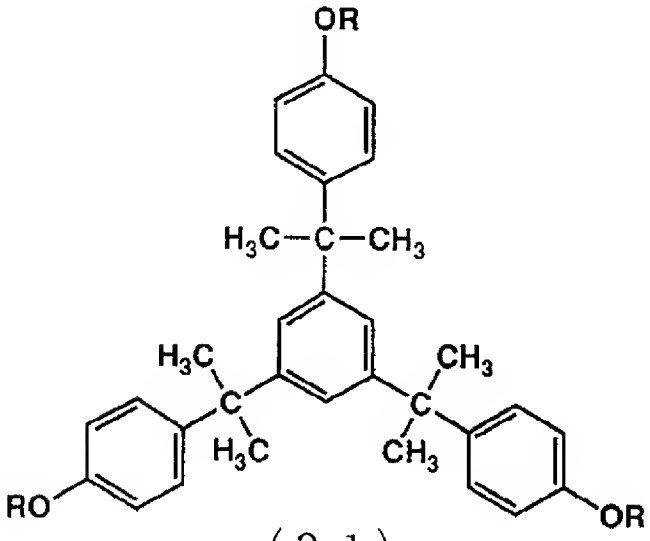
(28)



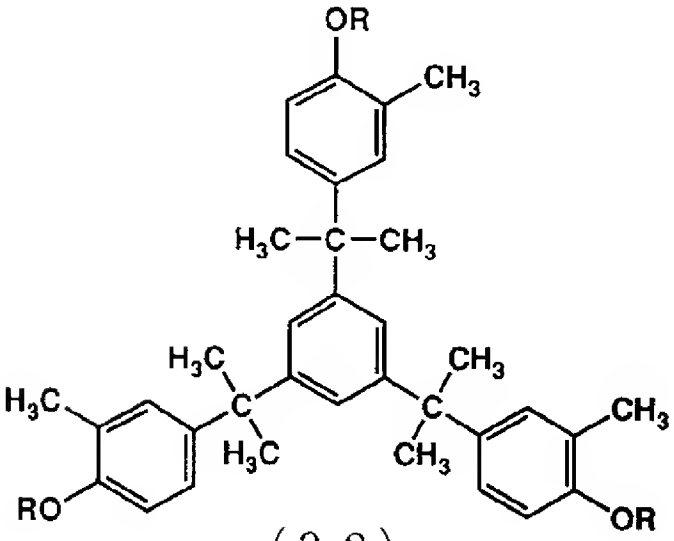
(29)


RO
RO
O
O
OR
OR

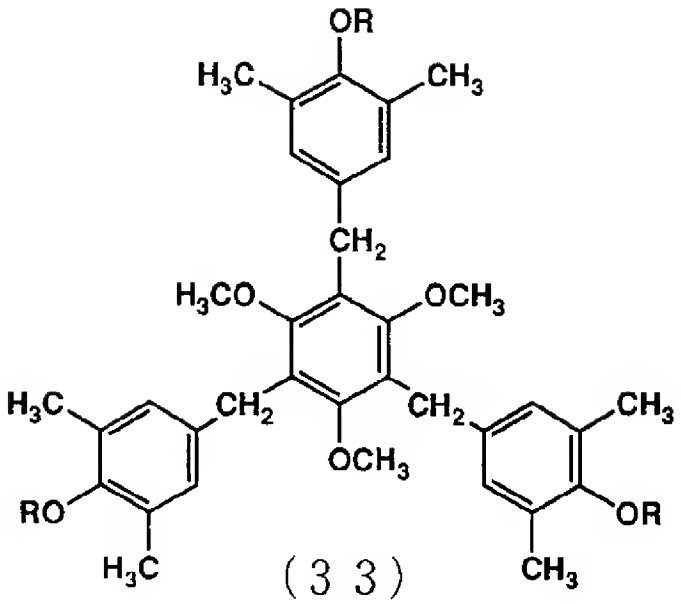
(30)


OR
H3C
C
CH3
H3C
C
CH3
H3C
CH3
RO
OR

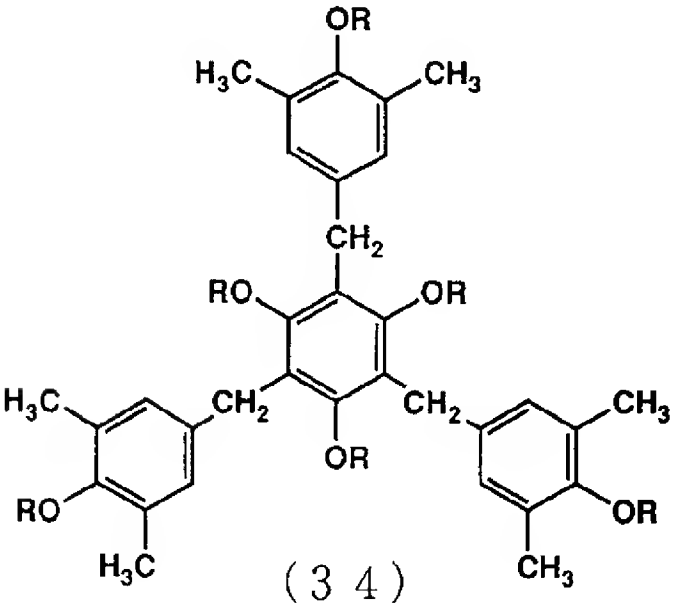
(31)


OR
CH3
H3C
C
CH3
H3C
C
CH3
H3C
CH3
H3C
CH3
RO
OR

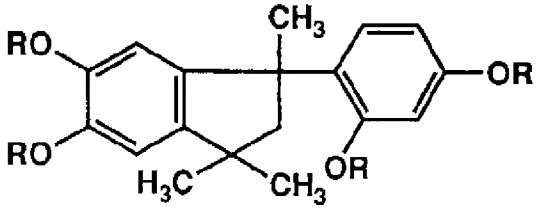
(32)



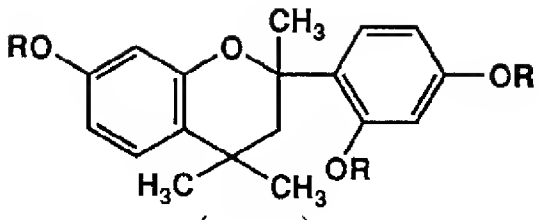
(33)



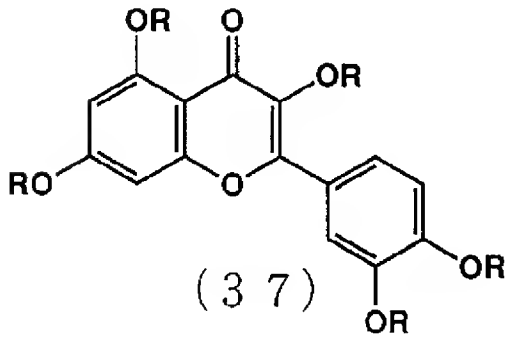
(34)



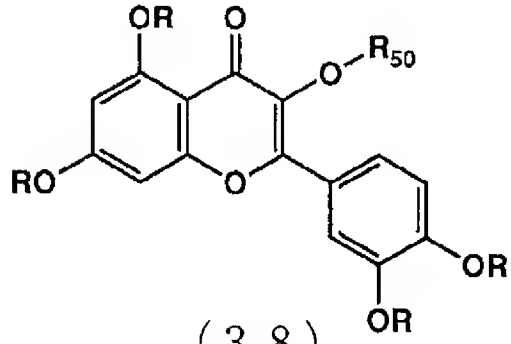
(35)



（３６）

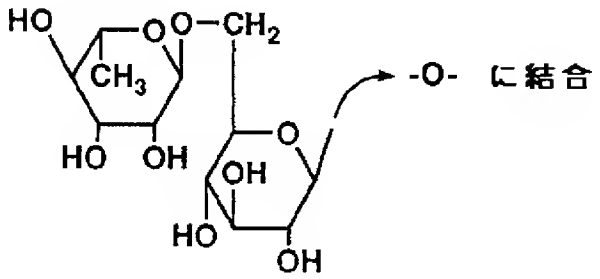


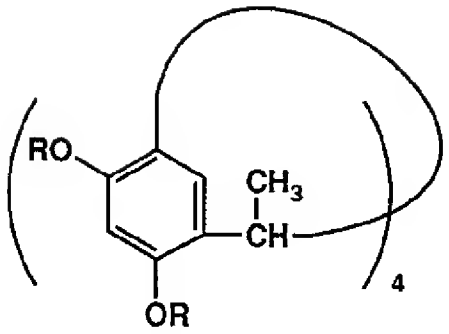
（３７）



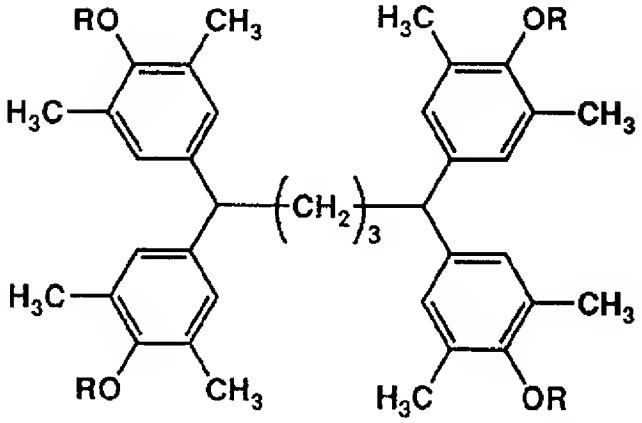
（３８）

但し、R_{50}:

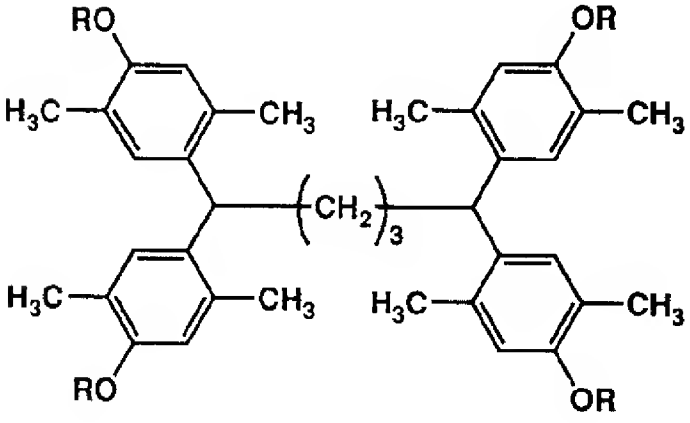



RO
CH3
CH
4
OR

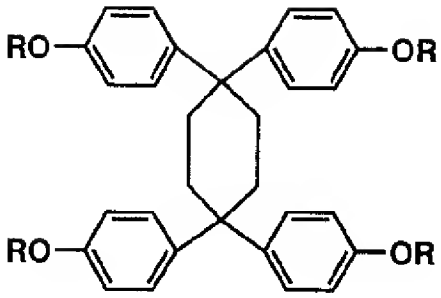
(39)


RO
CH3
H3C
OR
H3C
CH3
(CH2)3
H3C
CH3
RO
CH3
H3C
OR

(40)


RO
OR
H3C
CH3
H3C
CH3
(CH2)3
H3C
CH3
H3C
CH3
RO
OR

(41)



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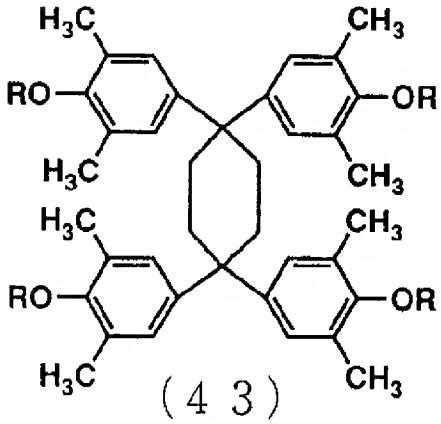
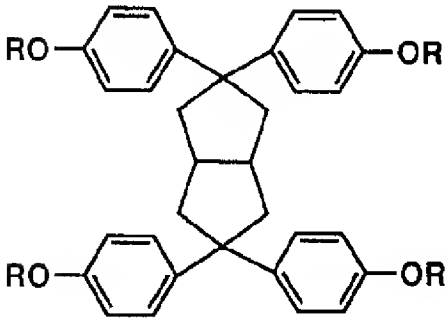
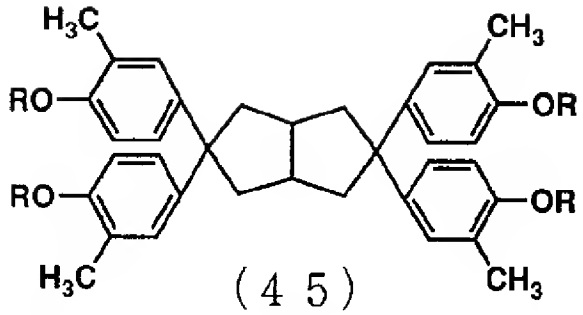


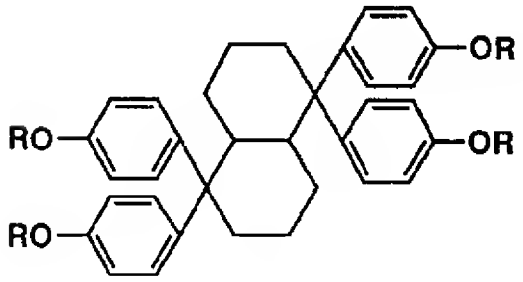
（４３）



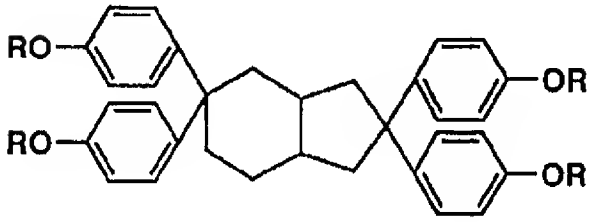
（４４）



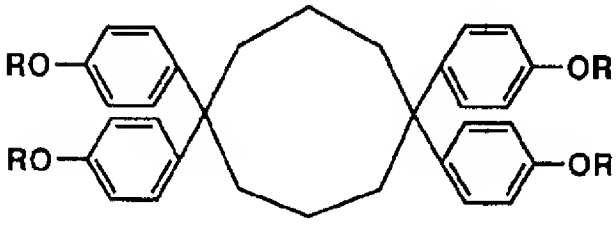
(45)



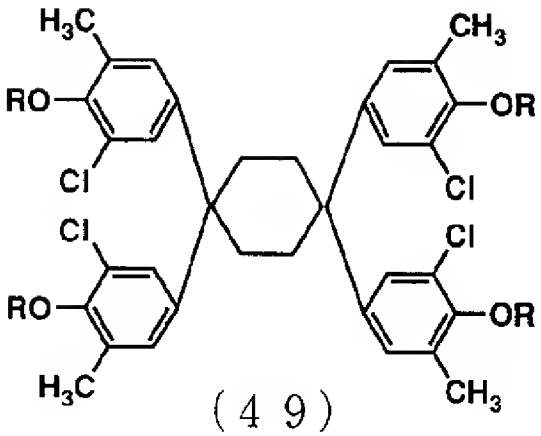
(46)



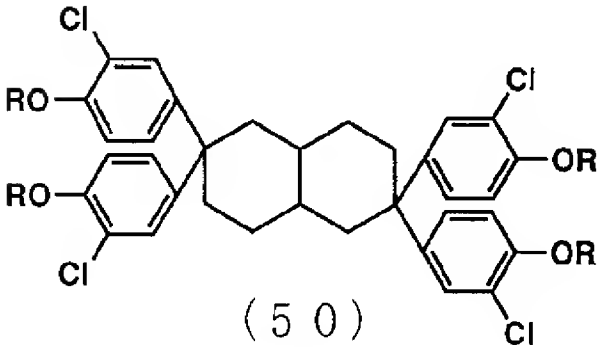
(47)



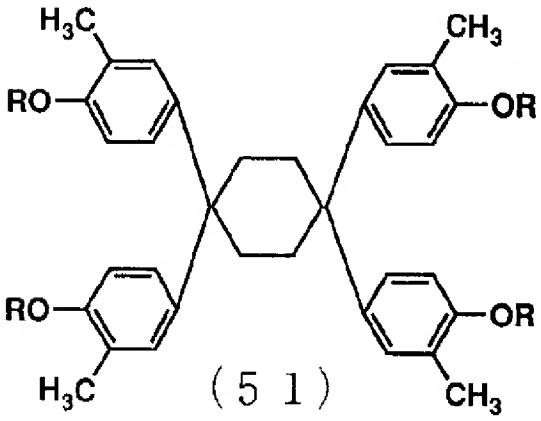
(48)


H3C
CH3
RO
OR
Cl
Cl
Cl
Cl
RO
OR
H3C
CH3

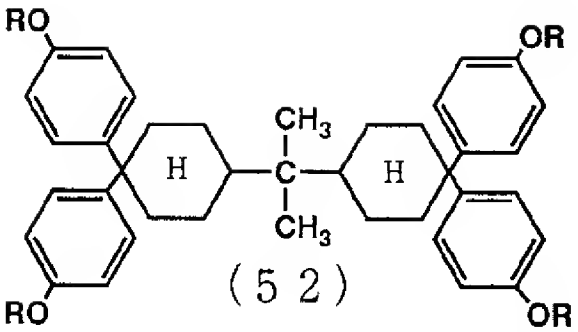
(49)


Cl
Cl
RO
OR
RO
OR
Cl
Cl

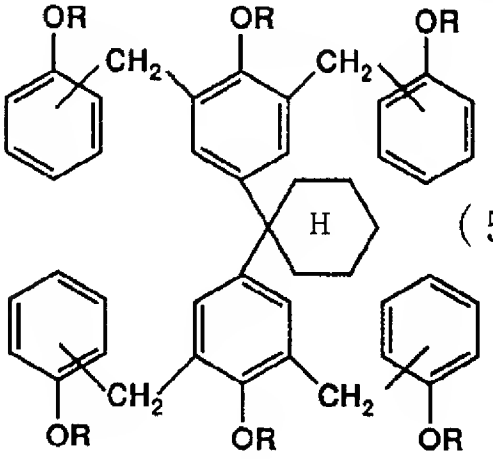
(50)


H3C
CH3
RO
OR
RO
OR
H3C
CH3

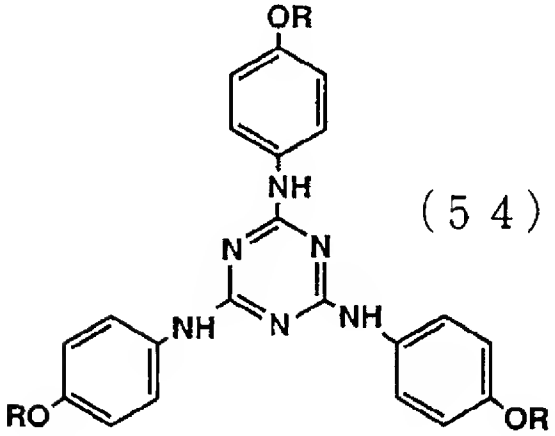
(51)


RO
OR
CH3
H
C
H
CH3
RO
OR

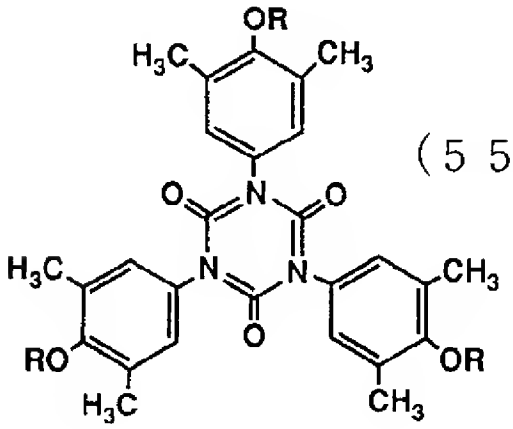
(52)


OR
OR
OR
CH2
CH2
H
CH2
CH2
OR
OR
OR

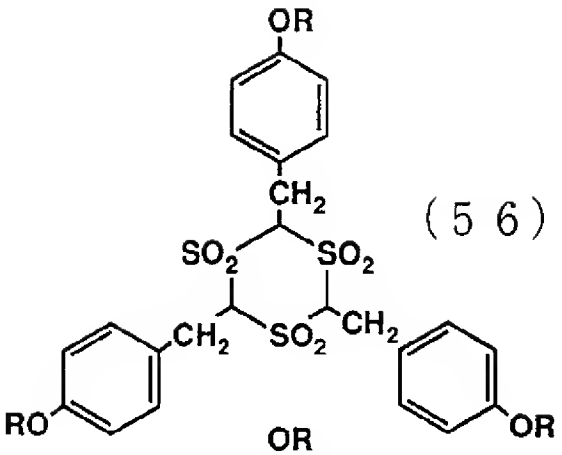
(53)


OR
NH
N
N
NH
N
NH
RO
OR

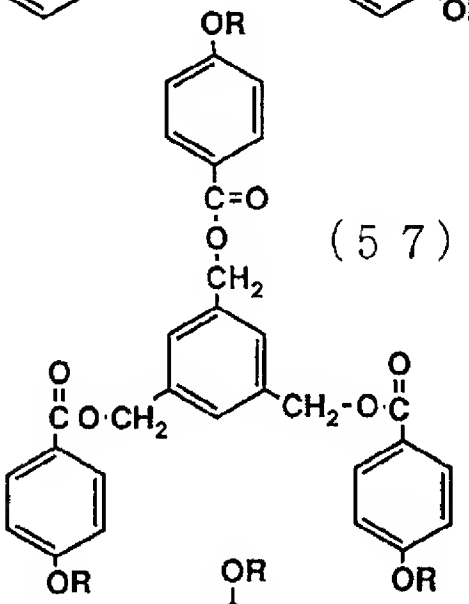
(54)


OR
H3C
CH3
O
N
O
H3C
N
N
CH3
O
RO
OR
H3C
CH3

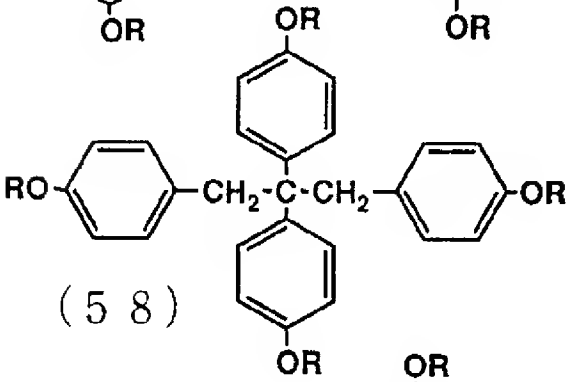
(55)



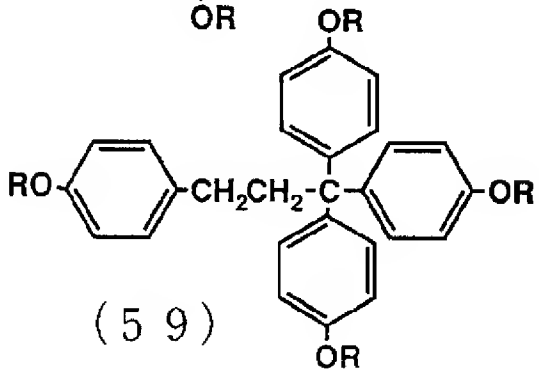
(56)



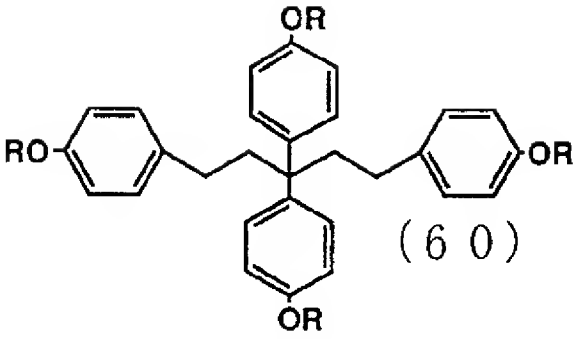
(57)



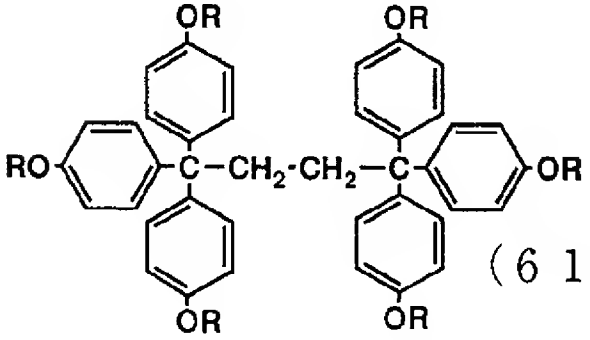
(58)



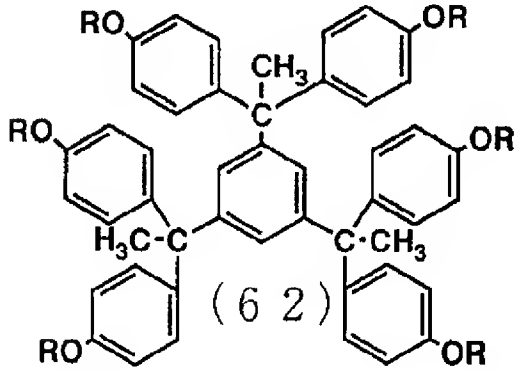
(59)


OR
RO
OR
OR

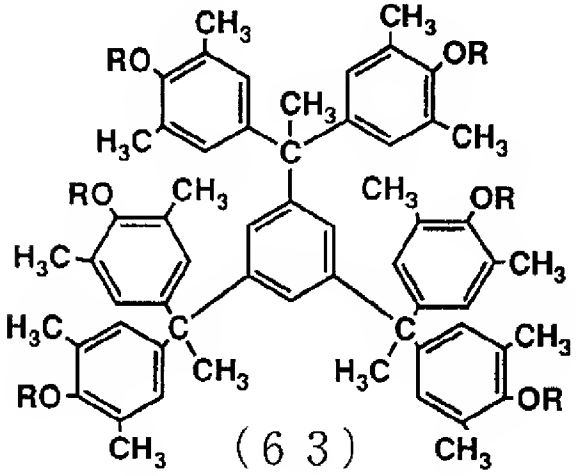
(60)


OR
OR
RO
C
CH2·CH2
C
OR
OR
OR

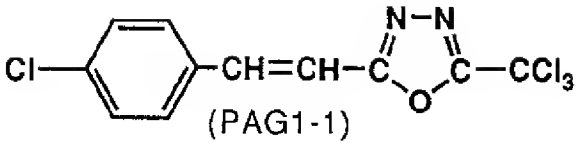
(61)


RO
OR
CH3
C
RO
OR
H3C-C
C·CH3
RO
OR

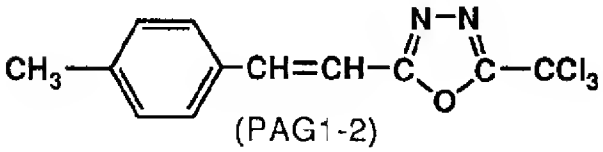
(62)


CH3
CH3
RO
OR
CH3
H3C
CH3
C
RO
CH3
CH3
OR
H3C
CH3
H3C
C
C
CH3
CH3
RO
H3C
OR
CH3
CH3

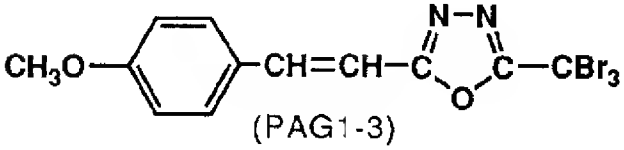
(63)



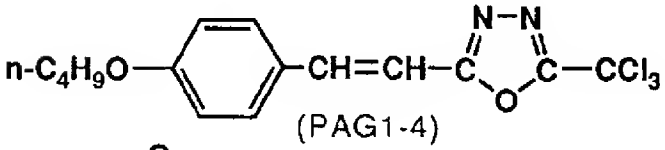
(PAG1-1)



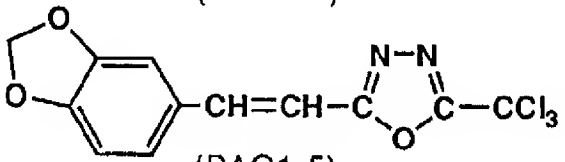
(PAG1-2)



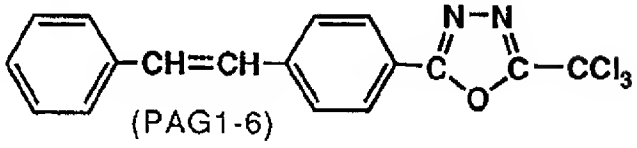
(PAG1-3)



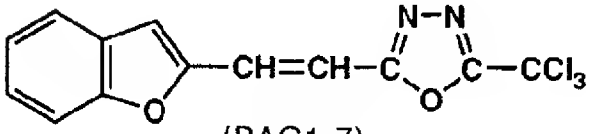
(PAG1-4)



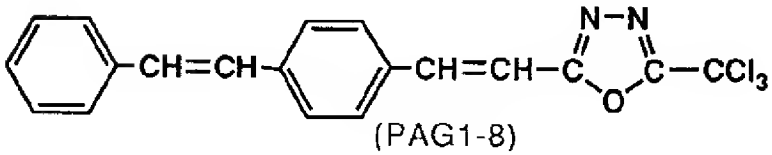
(PAG1-5)



(PAG1-6)



(PAG1-7)



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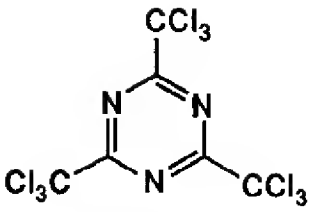

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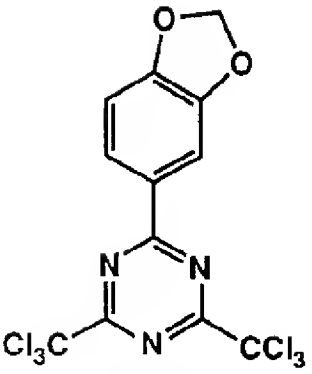

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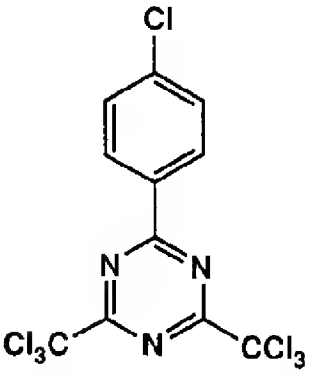

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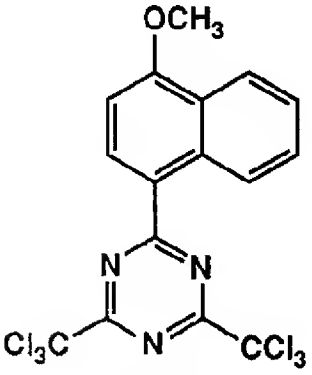

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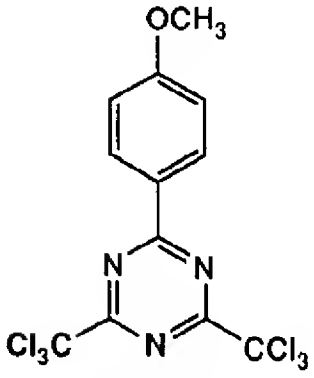

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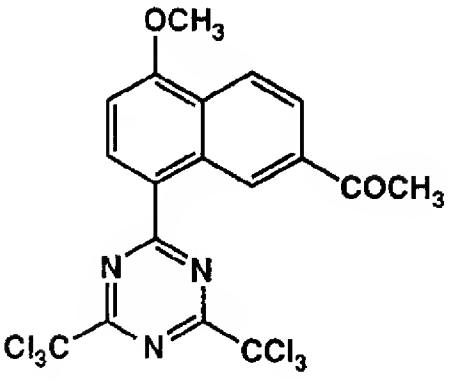

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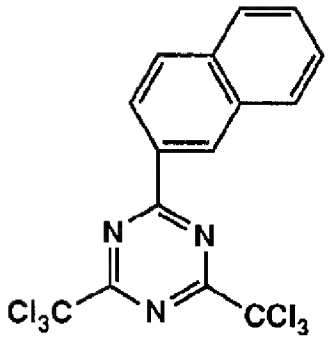

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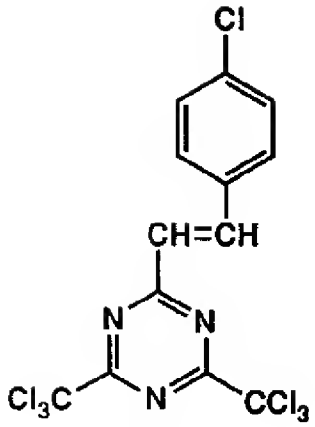

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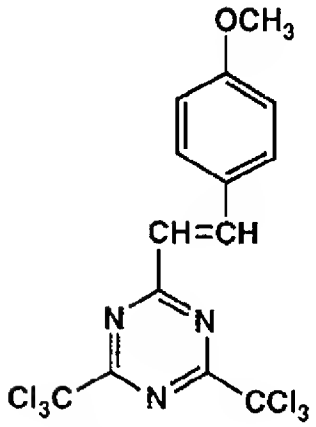

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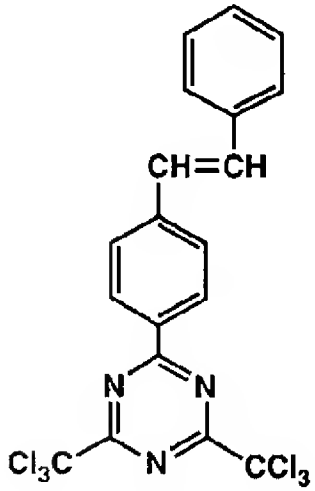

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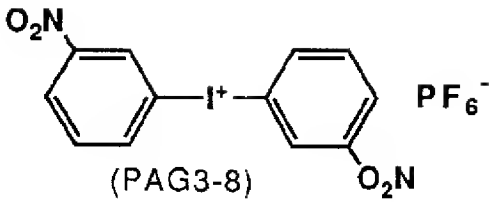

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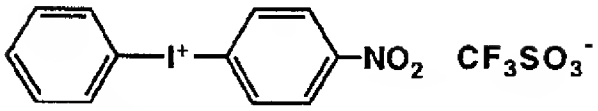

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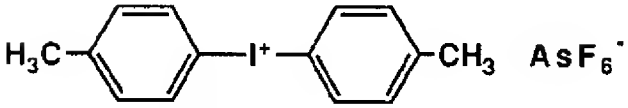

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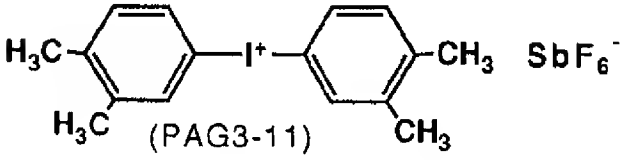

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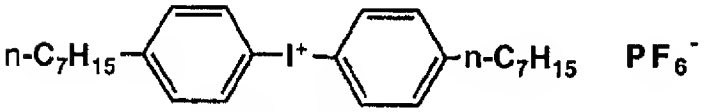

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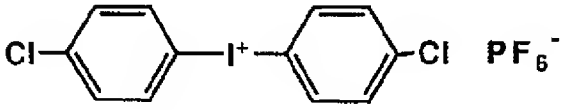

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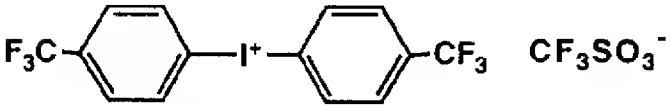

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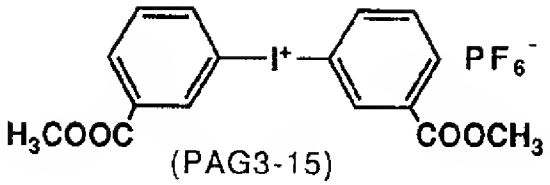

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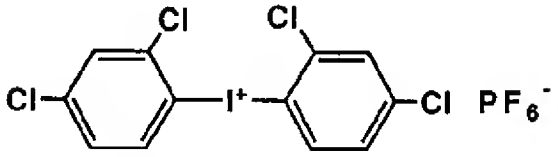

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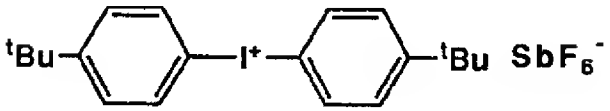

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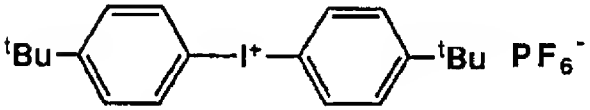

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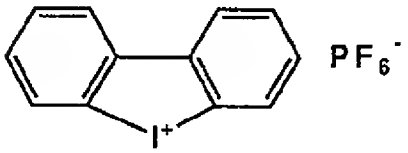

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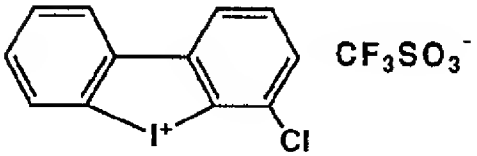

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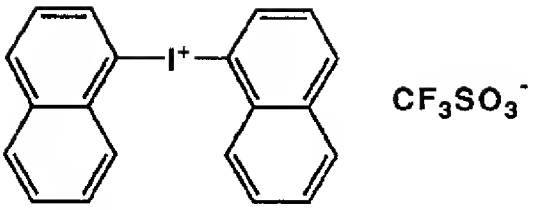

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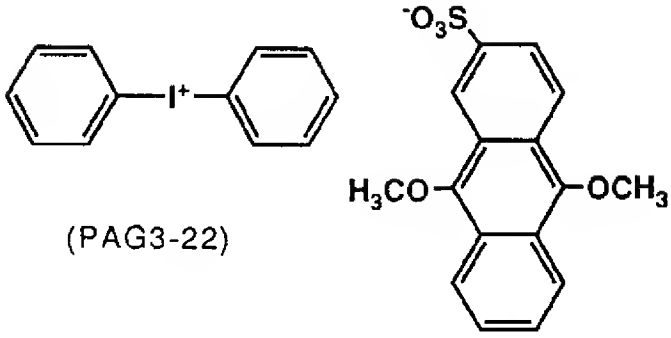

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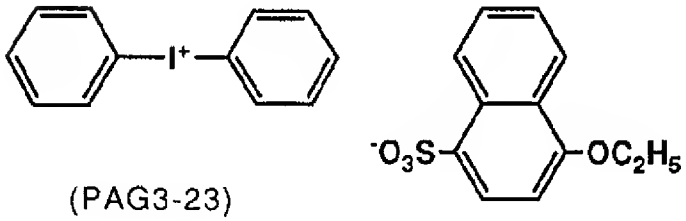

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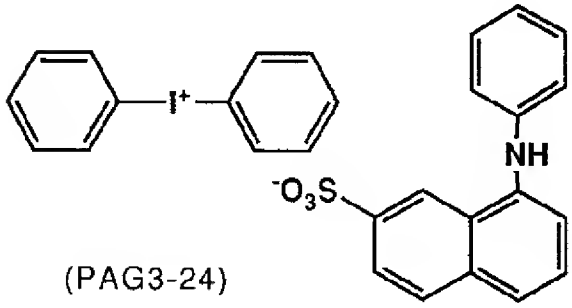

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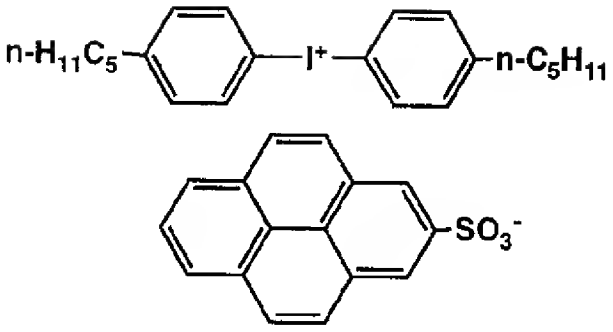

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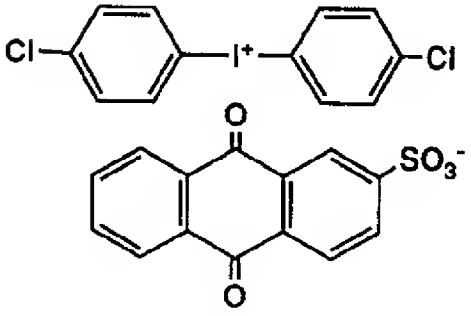

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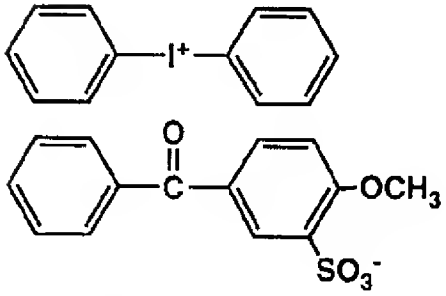

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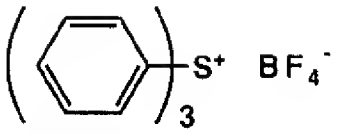

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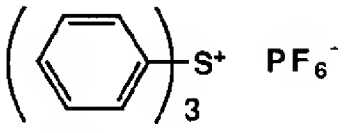

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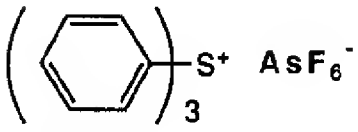

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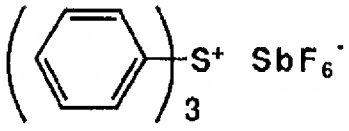

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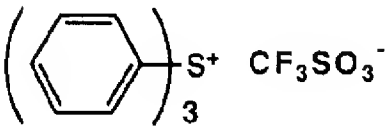

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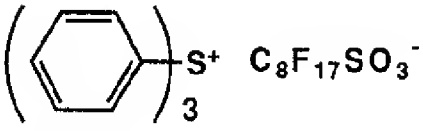

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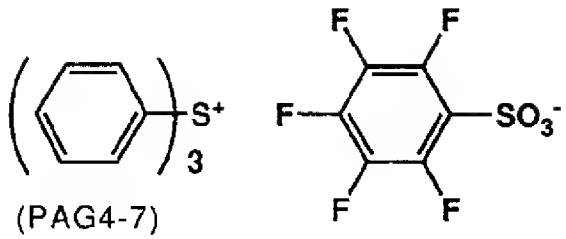

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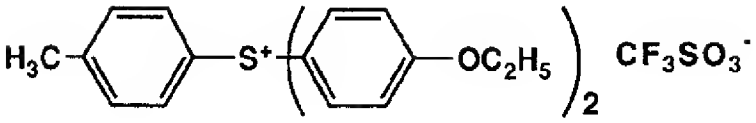

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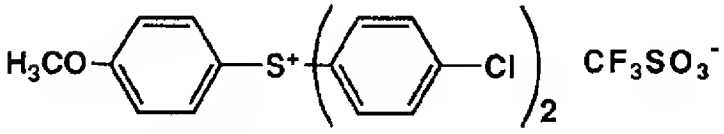

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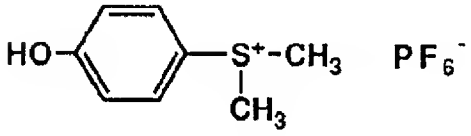

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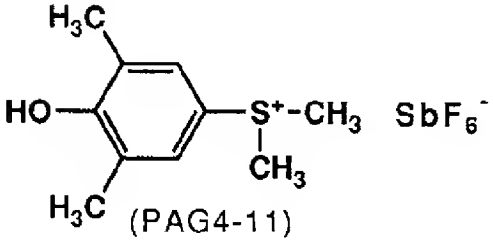

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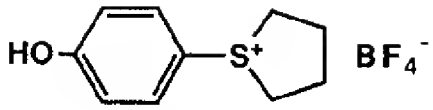

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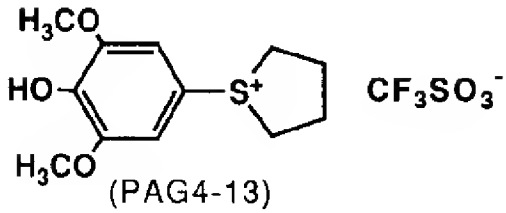

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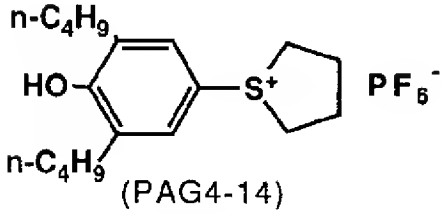

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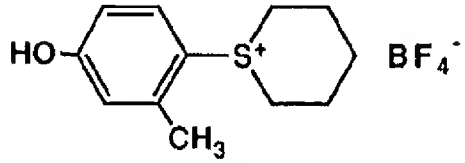

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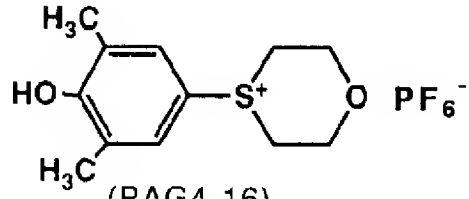

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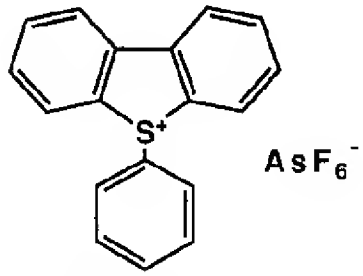

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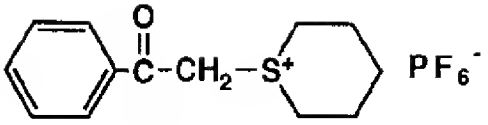

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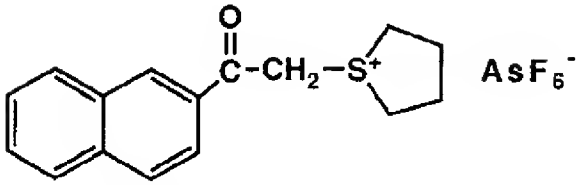

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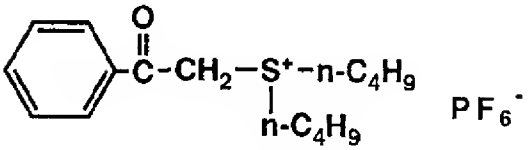

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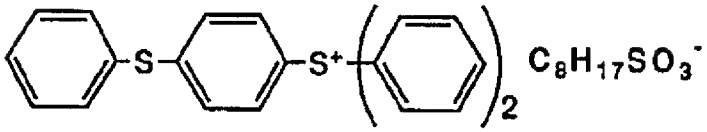

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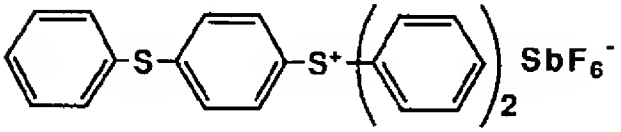

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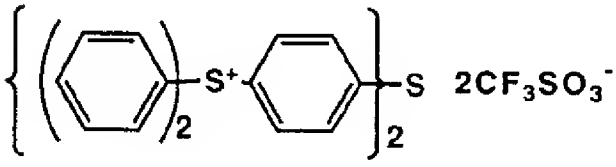

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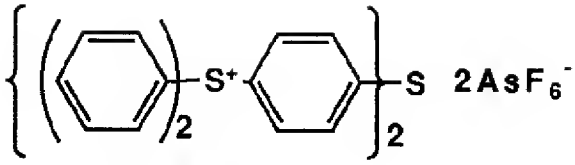

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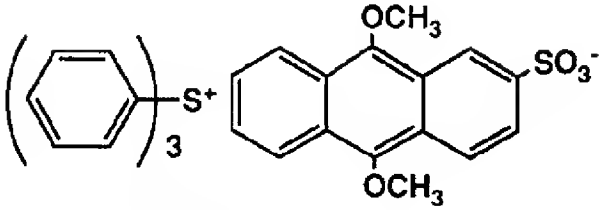

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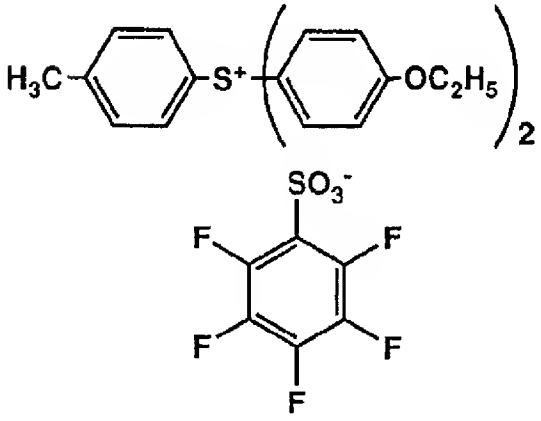

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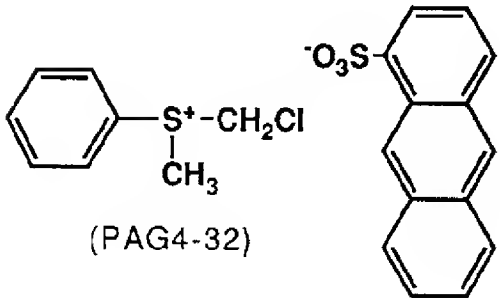

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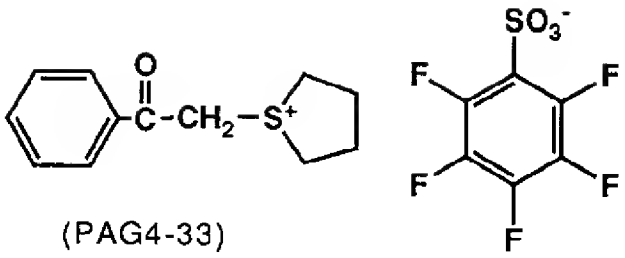

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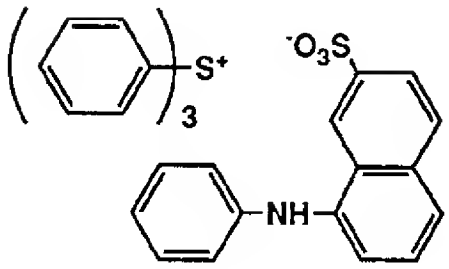

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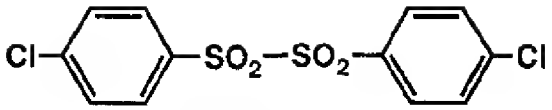

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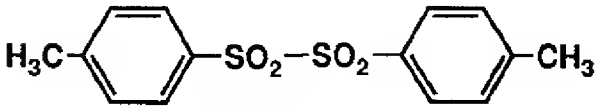

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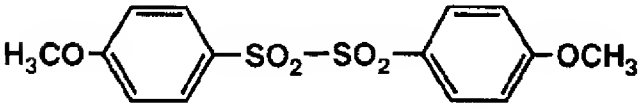

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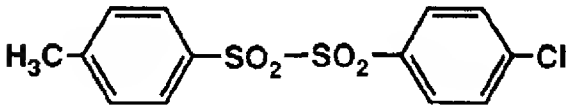

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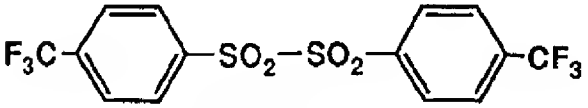

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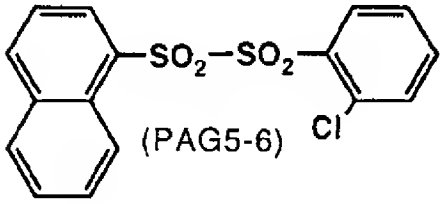

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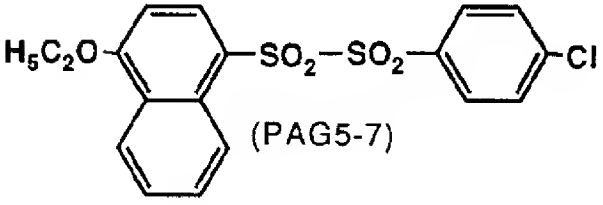

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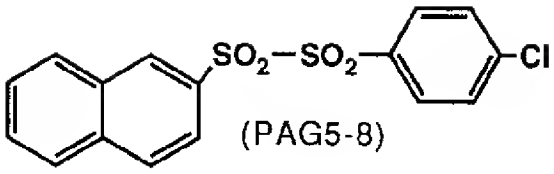

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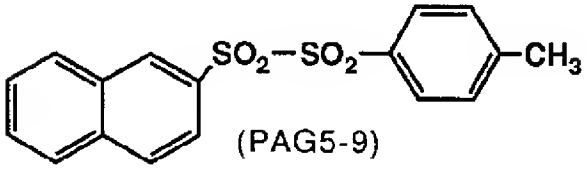

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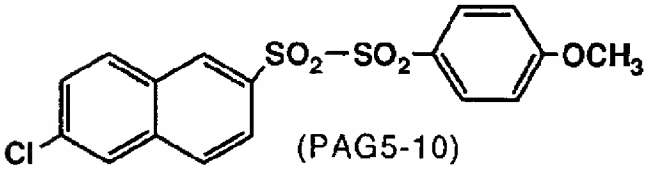

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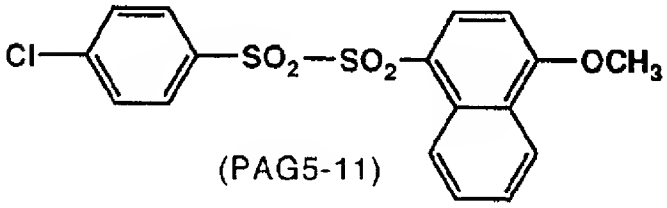

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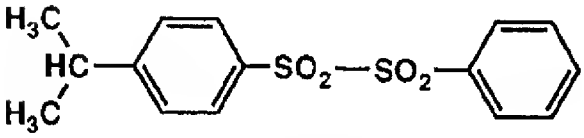

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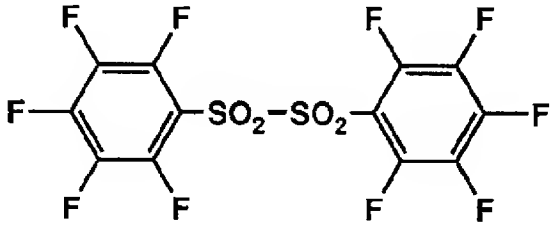

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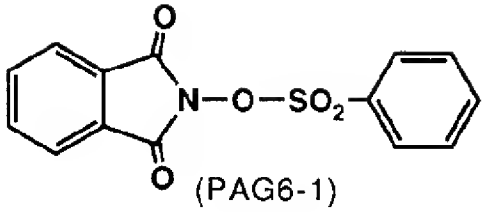

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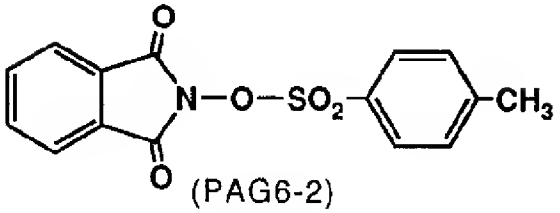

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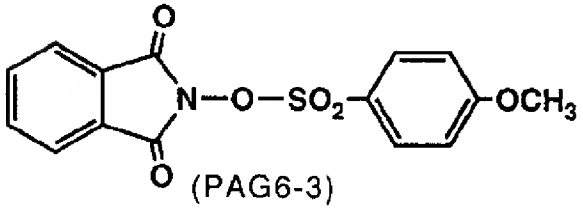

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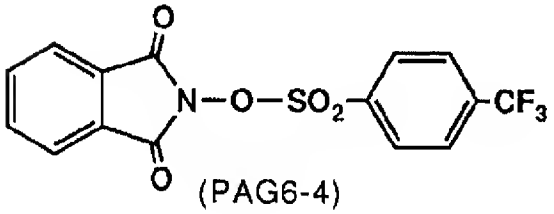

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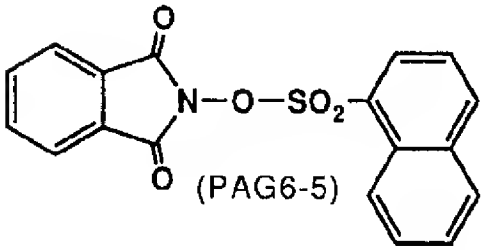

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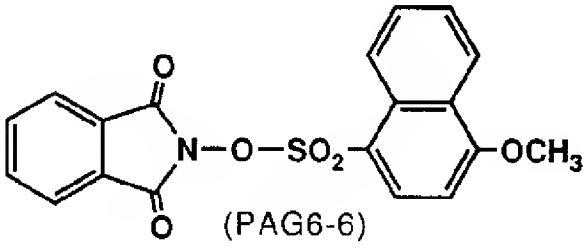

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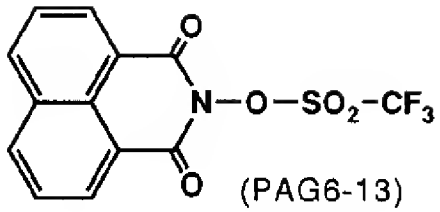

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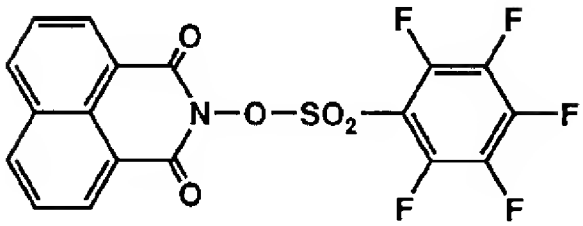

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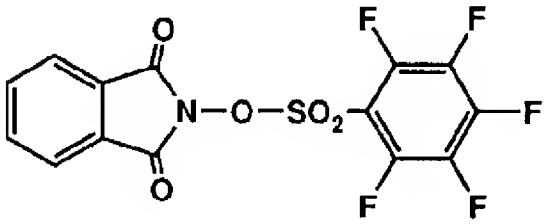


(PAG6-15)

表1：感光性組成物の処方

	アルカリ可溶性樹脂(g)		光酸発生剤(g)		溶解阻止剤(g)		酸分解性基	溶剤(重量比)
実施例 1	NOV.7	1.5	PAG3-3	0.05	化合物(1)	0.55	TBOC	MMP
実施例 2	NOV.6	1.5	PAG4-3	0.05	化合物(6)	0.55	TBE	PGMA
実施例 3	NOV.4	1.5	PAG4-5	0.05	化合物(10)	0.55	THP	EL/EEP = 6/4
実施例 4	NOV.3	1.5	PAG4-7	0.05	化合物(10)	0.55	TBE	HP
実施例 5	NOV.5	1.5	PAG4-5	0.05	化合物(12)	0.55	CUE	PGMA
実施例 6	NOV.2	1.5	PAG4-4	0.05	化合物(18)	0.55	TBE	MMP/DEGDM = 8/2
実施例 7	NOV.6	1.5	PAG5-4	0.05	化合物(18)	0.55	THP	PGMA
実施例 8	NOV.2	1.5	PAG5-12	0.05	化合物(19)	0.55	TBOC	MMP
実施例 9	NOV.4	1.5	PAG6-15	0.05	化合物(25)	0.55	TBOC	HP
実施例 10	NOV.1	1.5	PAG4-4	0.05	化合物(29)	0.55	CUE	PGMA/DEGDM = 7/3
実施例 11	NOV.3	1.5	PAG4-3	0.05	化合物(31)	0.55	TBOC	MMP
実施例 12	NOV.3	1.5	PAG4-3	0.05	化合物(31)	0.55	TBE	PGMA
実施例 13	NOV.1	1.5	PAG4-5	0.05	化合物(40)	0.55	TBOC	EL/DEGDM = 8/2
実施例 14	PVP	1.5	PAG4-7	0.05	化合物(44)	0.55	TBE	MMP
実施例 15	NOV.3	1.5	PAG6-2	0.05	化合物(60)	0.55	TBE	HP/DEGDM = 7/3
実施例 16	PVP	1.5	PAG4-6	0.05	化合物(60)	0.55	TBOC	PGMA/DEGDM = 7/3
実施例 17	PVP	1.5	PAG4-5	0.05	化合物(62)	0.55	TBE	PGMA
実施例 18	NOV.3	1.5	PAG4-5	0.05	化合物(31:合成例6)	0.55	TBOC	PGMA
実施例 19	NOV.2	1.5	PAG4-5	0.05	化合物(31:合成例7)	0.55	TBE	MMP
比較例 1	NOV.3	1.5	PAG4-3	0.05	化合物(31)	0.55	TBE	THF
比較例 2	NOV.3	1.5	PAG4-3	0.05	化合物(31)	0.55	TBOC	IBB
比較例 3	NOV.3	1.5	PAG4-3	0.05	化合物(31)	0.55	TBE	NMP
比較例 4	TBOCS	1.0	PAG4-3	0.1	—		—	PGMA
比較例 5	TBAMS	1.0	PAG4-3	0.1	—		—	PGMA
比較例 6	NOV.3	1.5	PAG4-3	0.05	DTBTP	0.55	—	PGMA
比較例 7	NOV.3	1.5	PAG4-3	0.05	TBP8P	0.55	—	PGMA
比較例 8	NOV.3	1.5	PAG4-3	0.05	TBNC	0.55	—	PGMA

TBOC : $-O\text{-}COO\text{-}C_4H_9{}^t$

TBE : $-O\text{-}CH_2\text{-}COO\text{-}C_4H_9{}^t$

CUE : $-O\text{-}CH_2\text{-}COO\text{-}C(CH_3)_2C_6H_5$

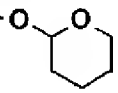
THP : 

表2：評価結果

	相対感度	現像による膜減り（%）	解像力（μm）	レジストパターンのプロファイル
実施例 1	1.2	2	0.34	良好
実施例 2	1.4	2	0.34	良好
実施例 3	1.3	2	0.35	良好
実施例 4	1.4	1	0.30	良好
実施例 5	1.2	1	0.35	良好
実施例 6	1.4	1	0.30	良好
実施例 7	1.1	2	0.34	良好
実施例 8	1.2	1	0.34	良好
実施例 9	1.2	1	0.35	良好
実施例 10	1.5	1	0.35	良好
実施例 11	1.4	1	0.30	良好
実施例 12	1.4	1	0.30	良好
実施例 13	1.4	1	0.32	良好
実施例 14	1.5	1	0.30	良好
実施例 15	1.2	1	0.30	良好
実施例 16	1.4	2	0.28	良好
実施例 17	1.4	1	0.30	良好
実施例 18	1.8	2	0.28	良好
実施例 19	1.8	2	0.28	良好
比較例 1	0.9	3	0.35	良好
比較例 2	1.4	4	0.37	ややテーパー
比較例 3	1.4	4	0.37	ややテーパー
比較例 4	1.0	4	0.40	テーパー
比較例 5	0.9	4	0.40	テーパー
比較例 6	1.1	15	0.45	テーパー
比較例 7	1.3	19	0.45	テーパー
比較例 8	1.3	23	0.47	テーパー